APPLIED RESEARCH, FABRICATION AND TESTING OF 2300°F THERMOCOUPLE FOR AIR-BREATHING PROPULSION SYSTEMS

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(Prepared Under Contract No. AF 33(616)-7825
by Engelhard Industries, Inc., Newark, New Jersey
by Herbert J. Greenberg and Edward D. Zysk)

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FOREWORD

This report has been prepared as the culmination of the work done under USAF contract No. AF 33(616)-7825. The contract was administered under the direction of the Propulsion Laboratory of Aeronautical Systems Division, Wright-Patterson Air Force Base, Ohio by Captain H. I. Bush and Mr. E. E. Buchanan.

Instruments and Systems Section supervised the joint industry project with Research and Development Division under the administrative guidance of Dr. M. A. Kashmiry, Chief Engineer, the coordination being handled by Mr. H. J. Greenberg, Project Engineer.

The three major tasks involving the metallurgy, wire manufacture, and materials testing were administered by Dr. H.J. Albert, Head of the Physics Department of the Research and Development Division. Mr. E. D. Zysk coordinated all phases of Task Nos. 1, 2, and 3, while also acting in liaison capacity with Instruments and Systems Section.

The development work on the thermocouple materials was done by Mr. D. J. Accino and Dr. J. F. Schneider. Others who contributed to the development were Messrs. D. Osterberg, E. Pan and D. Toenshoff, all of the Research and Development Division.

Mr. J. S. Hill directed the experimental work done on the Fibro materials with the assistance of Mrs. J. Wisely.

Mr. H. J. Greenberg was responsible for direction of the Task No. 4 effort covering manufacturing techniques and production of hardware. Messrs. J. Clay and M. Skal of the Instruments and Systems Section made significant contributions in this phase of the work.

Mr. D. Campbell performed the initial testing on thermocouple probes submitted to the Propulsion Laboratory, Aeronautical Systems Division.

The stimulating assistance of Mr. F. R. Caldwell, Chief of Combustion Controls Section at the National Bureau of Standards, Washington, D. C., is gratefully acknowledged. Mr. Lief O. Olsen and Mr. P. D. Freeze also contributed to the testing of the various probes submitted for thermal response and temperature cycling tests.

ABSTRACT

Applied research work on two thermocouple systems for use in aircraft jet engines to temperatures of 2300°F is herewith reported. The two couples involved are the palladium vs. platinum 15% iridium previously investigated under USAF contract No. AF 33(600)-32302, and Platinel 2, a proprietary material produced by Engelhard Industries, Inc.

Reliability of the latter thermocouple in the jet engine environment is shown.

Fabrication technique for manufacture of four basic thermocouple geometries as well as performance data for same are presented.

(85 pgs)(29 ref)(34 figs)(21 tbls)

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INTRODUCTION

The work performed on this contract was an outgrowth of the development of the thermocouple system of palladium vs. platinum 15% iridium which was initially explored under Air Force contract AF 33(600)-32302 and reported in ASD Technical Report 57-744, published in January, 1959. This thermocouple has the advantage of having a high output, approximately 75% of the lower temperature chromel vs. alumel system.

Present in-production turbo-prop and turbo-jet engines utilize chromel vs. alumel thermocouple systems for sensing turbine inlet and exhaust gas temperatures. Such systems will not be satisfactory for future high temperature turbine engine propulsion systems due to the inherent characteristics of the materials. Temperature sensing systems with thermocouple elements of the noble metal family can withstand the high temperature environments anticipated. The main deficiency of the older noble metal combination, namely platinum vs. platinum-rhodium and iridium vs. iridium-rhodium, is the relatively low output which imposes severe amplification problems on the engine control system. It was toward this purpose that the applied research, fabrication and testing of the palladium vs. platinum 15% iridium material investigated further under this contract were directed.

A parallel investigation on a new material known as Platinel 2 (reference 6) was authorized by the terms of this contract. This material had been developed to the point that it showed interesting properties with respect to gas turbine measurement requirements, warranting further investigation to meet the goals of the contract. Some work in adapting this material to existing turbo-prop engines had already been done by the Allison Division of the General Motors Corporation.

The investigative work was sub-divided into four tasks, Nos. 1, 2 and 3 of which comprise all of the metallurgical and applied research performed on both the palladium vs. platinum 15% iridium, and the Platinel 2 thermocouple materials. Task No. 4 was concerned with the fabrication and development of techniques for manufacture of the items of test hardware required by the terms of the contract. It also covered those tests which were performed within the laboratory of the instru-

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ments and Systems Section prior to shipment of the probes.

The evaluation testing consisted of initial calibration, checks for response time, susceptibility to thermal-shock, and insulation resistance, and the effects of fuel contamination in swaged samples were also checked.

Testing of samples hardware was started at the Propulsion Laboratory of Aeronautical Systems Division, Wright Field. The equipment at the division was limited to continuous operation at 2000°F. Some considerable number of hours of thermal shock cycling time were accumulated prior to malfunction of the compressor and subsequent burn-out of the exhaust stack. All thermal shock cycling tests were subsequently performed at the laboratories of the National Bureau of Standards in Washington, D. C.. Time response tests were likewise performed at the National Bureau of Standards.

The work performed by the Bureau is reported in ASD-TDR-62-835. This work was done under separate contract of NBS with ASD under Air Force Contract No. AF 33(616) 61-01. Certain information, especially in regard to thermal response time, incorporated within this report, has been taken out of context from the NBS report.

Scope of Program

A parallel applied research of the palladium vs. platinum 15% iridium and Platinel 2 thermocouple materials for the purpose of meeting certain performance goals was followed during the early stages of the work. The Statement of Work of the contract assumed that system life of the Pd vs. Pt15Ir couple was the result of "fatigue failures of the junction", and authorized intensive investigations to meet the performance goals through improved design, materials, processes, and techniques. The performance goals included:

1. Steady state temperature range 0-2300°F.

2. Maximum transient temperature limit - 2500°F.

3. A maximum spread in emf output of all thermocouples delivered on this procurement not exceeding ±0.5% of the mean calibration curve.

4. A constancy of calibration within ±0.5% after exposure to thermal shock cycles from 80°F to 2000°F at a mass flow rate of 13 lbs. per sq. ft. per second.

5. A time of response for open junction thermocouples of 1.2 seconds at a gas flow rate of 6 lbs. per sq. ft. per second.

6. Insulation resistance of at least 100,000 ohms under all high temperature and storage conditions.

The following four tasks were undertaken to serve as a foundation to enable meeting the performance goals.

Task No. 1

1. (a)

Melting Point Determination of Platinel 2 Alloys 1813 and 1503

(b)

Life Testing of Platinel 2.

(c)

Resistivities of Individual Legs of Platinel 2 Thermocouple.

(d)

Mechanical Properties at High Temperature.

(e)

Effect of Various Temperatures at the Junction of Platinel 2 and Chromel-Alumel Leadwires on the emf Output of the Thermocouple.

2. Investigate the Ability of Platinel 2 to Match Chromel-Alumel to 1500°F (816°C)

Task No. 2

1. Manufacture of Palladium vs. Platinum 15% Iridium Wire.

Task No. 3

1. Investigate the Value of Use of Fibro on Reliability, Endurance, and Accuracy of Calibration Over Life in the Palladium vs. Platinum 15% Iridium Thermocouple as well as in Platinel 2.

Fibro, a proprietary process, described in Appendix II was developed to inhibit grain growth in pure metals. U. S. Patent No. 3,049,577 covering this process has been issued to Engelhard Industries, Inc..

The two major areas in which the two thermocouple systems were investigated were life testing and determination of mechanical properties at high temperature.

Life Testing

A. Platinel 2

1. At 600, 800, 1000, 1200 and 1300°C for about 1000 hours.

(a) In air

(b) In hydrogen

B. Fibro Platinel 2

1. At 1260°C for 1080 hours

(a) In air

C. Fibro Pd vs. Pt15% Ir

1. At 1260°C for 1080 hours

(a) In air

Mechanical Properties at High Temperature

Hot tensile tests and stress-to-rupture tests at 800, 1000, and 1200°C were performed on:

1. 1503
2. 1813
3. Fibro 1503
4. Fibro 1813
5. Palladium
6. Fibro palladium
7. Platinum-15% iridium

Task No. 4

This phase of the contract covered the development of manufacturing techniques and fabrication of all hardware delivered to Aeronautical Systems Division and The National Bureau of Standards. Four specific probe geometries were proposed and investigated. These were:

1. A stirrup-type junction.
2. A V-type junction having wires of tapered cross-section.
3. A beaded V-type junction.
4. A coaxial or "pencil" type junction.

All but the last type of construction were produced in palladium vs. platinum 15% iridium as well as Platinel 2; Fibro couples of both thermocouple systems were fabricated also. The coaxial thermocouple was manufactured only in Platinel 2, the positive leg being in the tubular sheath.

Summary of Results

1. Thermal cycling tests performed at the National Bureau of Standards with a single burner test rig burning gasoline proved the inadequacy of Pd vs. Pt15%Ir to withstand the environment for any appreciable period of time. In 7 sample probes submitted for test, wire failures in the bare junction area occurred in all probes during the early stages of testing. Almost invariably, the failure exhibited itself in an "open" in the palladium element at any point between the junction and ceramic insulation. This break was always accompanied by pronounced elongation of this leg.

   Strong indications of contamination of the palladium by sulfur have been obtained by assay analysis.

2. The use of Fibro as a means of inhibiting grain growth and increasing the rupture strength of the palladium leg, it was hoped, would offer a solution to the odd behaviour of the pure palladium material under high temperature exposure to combustion gases. Unfortunately, no improvement in performance was shown through the use of this approach.

3. The palladium vs. platinum 15% iridium couple has given good indication of offering satisfactory service to 1300°C (2372°F) in an air environment under controlled laboratory conditions. Stability of emf output over long period of life is shown by the data.

4. The ability of the Platinel 2 alloys 1813 and 1503 to serve as a high temperature thermocouple to at least 1093°C (2000°F) in an engine environment has been clearly demonstrated. Metallurgical integrity of these wires in the bare junction area was shown by thermal cycling tests in a JP-4 fuel and air combustion atmosphere performed in a single burner test rig at Wright Patterson Air Force Base. At no time during similar tests with gasoline, as the fuel at the National Bureau of Standards, were there any junction failures. Internal wire failures within the packed ceramic insulation were noted in samples having reduced wire cross-section (.025 dia. compared to junction wire diameters of .040 and .032).* These failures were eliminated when wire cross-section was increased to .032 diameter within the body of the probe.

5. The employment of chromel and alumel base metal thermocouple materials as compensating leadwires for the Platinel 2 thermocouple system has been satisfactorily demonstrated at noble-to-base metal junction temperatures to 850°C.

* Reduction of wire cross-section was effected by drawing, swaging, or welding.

6. Melting point determinations for Platinel 2 alloys 1813 (+) and 1503 (-) were made. The useful temperature limit of the couple is controlled by the negative leg which has a solidus of 1426°C (2599°F).

7. Electrical resistivities of the Platinel 2 alloys 1813 and 1503 were individually measured at temperatures to 1200°C. The value for the 1813 alloy is approximately 50% greater at 1200°C than that of the 1503.

8. Stress-to-rupture and hot tensile test data for the various alloys investigated under the program are given - both for the regular as well as Fibro wires. Where Fibro platinum shows marked advantages over regular wire, little advantage is offered by the fibrous wire structure in the materials investigated, and then only in the pure palladium material at temperatures below 1000°C. No advantage in its use insofar as increasing stress-to-rupture or hot tensile strength in Platinel 2 is offered. The ability of Fibro to inhibit grain growth during thermal shock tests has not been investigated.

9. Four basic thermocouple probe geometries were studied as far as response time and thermal shock resistance are concerned. All of the basic constructions were satisfactory from a response time standpoint, the target being 1.2 seconds for 63% response; high thermal diffusivity of the noble metal couples of either the Pd vs. Pt15%Ir or Platinel 2 variety affords the attainment of response times of less than one second.

10. Experimental tests for response and thermal shock resistance on the last type of construction studied under this contract gave interesting results, showing a high order of structural rigidity for this couple. The "pencil" or coaxial construction responded to a step change of temperature slightly slower than conventional two-wire couples. Reduction of outer diameter from the .080 inches would undoubtedly improve the response time.

DESCRIPTION OF TASKS

Task No. 1

1 (a). Melting Point of Platinel 2 Alloys, 1503 and 1813

A. Objective

To determine the melting points of Platinel 2 alloys 1503 and 1813.

B. Equipment

The furnace used in making the melting point determinations is capable of reaching 2700°C and is shown in Figure 1. Figure 2 shows the top view of the interior (with cover removed), the top of the crucible, and the Pt vs. Pt10Rh thermocouple. The heating element is made of tungsten, and this made it necessary that all heating operations be carried out in an inert atmosphere.

The couple was calibrated against a standard couple that had been previously calibrated at the National Bureau of Standards. Two Rubicon B potentiometers and the necessary galvanometers were used in the calibration. A Honeywell Brown Electronik Recorder was used to plot the time-temperature curves from which the liquidus and the solidus temperatures were determined.

C. Experimental Method

The original plan called for the determination of the melting points by the wire method. However, before any work was started, it was decided to utilize a more accurate method, i.e., time-temperature heating and cooling curves.

The basic principle of the latter method is that the transition of a metal from one physical state to another, i.e., from solid to liquid, brought about by heating at constant pressure, is accompanied by an absorption of heat at the temperature where such a transformation occurs. On the other hand, when going from one physical state to another by cooling, the temperature at which the phase transformation takes place is accompanied by an evolution of heat. The explanation for this is that phases which are stable at high temperatures have a relatively higher energy content than those stable at lower temperatures. The transition point may be shown graphically by plotting the temperature rise or decrease vs. the time of heating, producing what is known as a time-temperature heating or cooling curve.

Figure 1. High Temperature Furnace

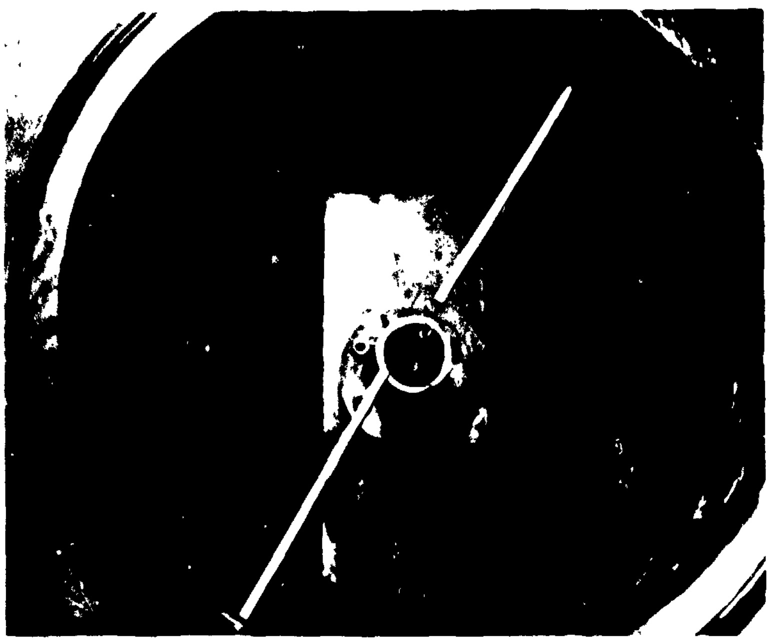

Figure 2. Top View Looking Into Furnace.
Cover Removed.

In this experiment a platinum vs. platinum 10% rhodium thermocouple was placed in the crucible containing the alloy to be tested (see Figure 2). The thermocouple was carefully positioned so that any temperature readings would be indicative of the metal temperature and not influenced by the wall of the crucible. The position of the couple was calculated and this position was governed by the volume of the metal after melting. The crucible and thermocouple were placed in the furnace, Figure 1, and the cover was put into place. The furnace was then evacuated and back filled with argon. After this was accomplished, the crucible was heated until the alloy melted. The crucible was then cooled until the metal was completely solidified. The test run was then started. Near the melting range, and just before it was reached, the crucible and melt were heated at a very slow (increasing) rate. The same procedure was used in the determination of the cooling curve.

Prior to use and immediately after use, the Pt vs. Pt10Rh thermocouple was calibrated against a standard couple. The calibration method used is similar to that described in Reference 12. See Appendix I for a description of the method and Figure 3 and Figure 4 for the equipment used in this testing.

Great care was taken in the setting up of the melting point determinations. Such factors as the wall thickness of the crucible, the amount of metal constituting the charge, and the rate at which the charge and the crucible were heated or cooled were all taken into account. Slow heating and cooling rates were used as well as a reasonably small charge.

D. Results

Platinel 1503	Liquidus	1447°C
	Solidus	1426°C
Platinel 1813	Liquidus	1608°C
	Solidus	1570°C

Three heating and cooling "runs" were made on each alloy. The data shown here are based on a weighted average.

1 (b). Life Testing of Platinel 2

A. Objective

Three Platinel 2 thermocouples, each from a different melt, were calibrated, tested at 600, 800, 1000, 1200 and

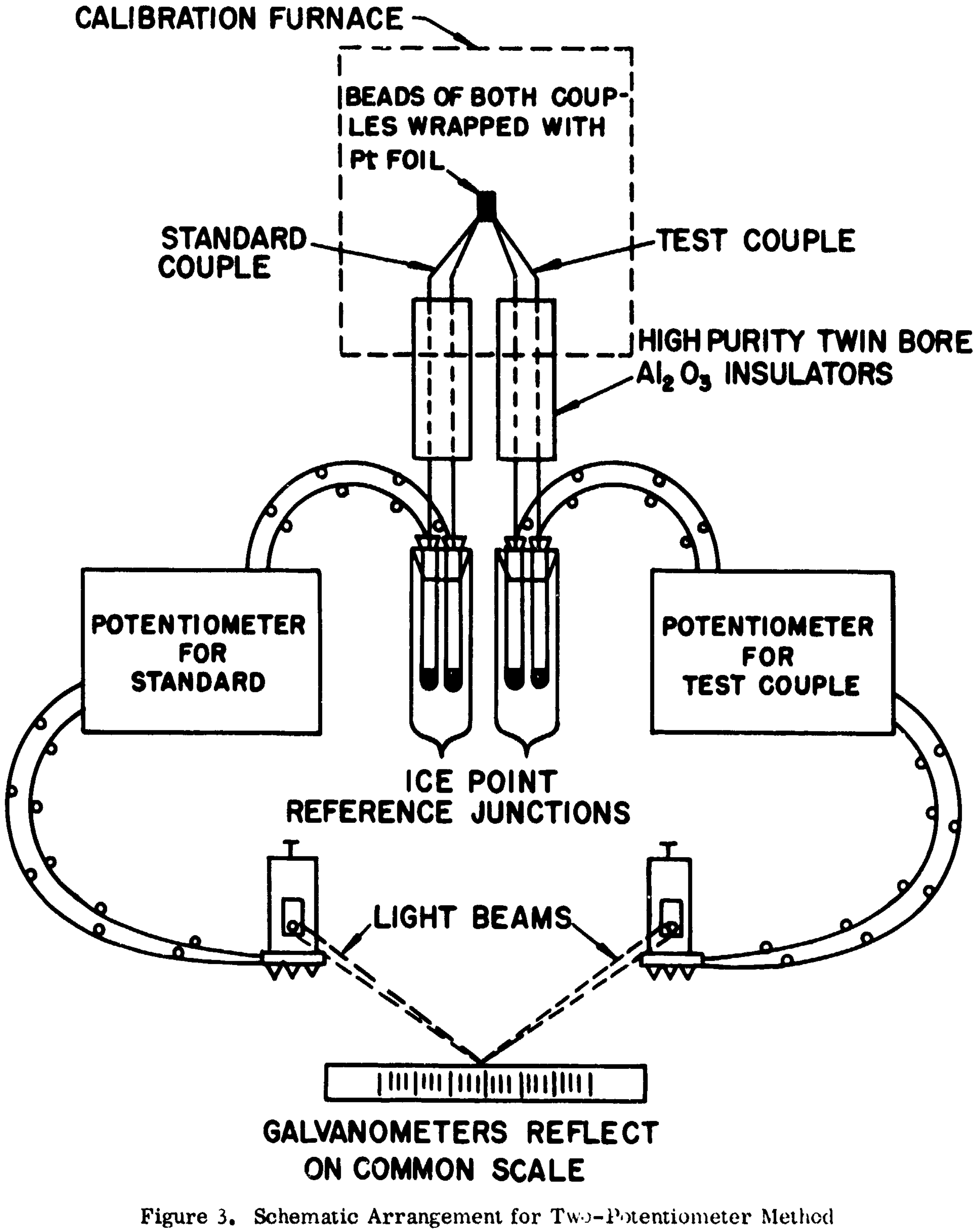

Figure 3. Schematic Arrangement for Two-Potentiometer Method for Calibration of Thermocouples

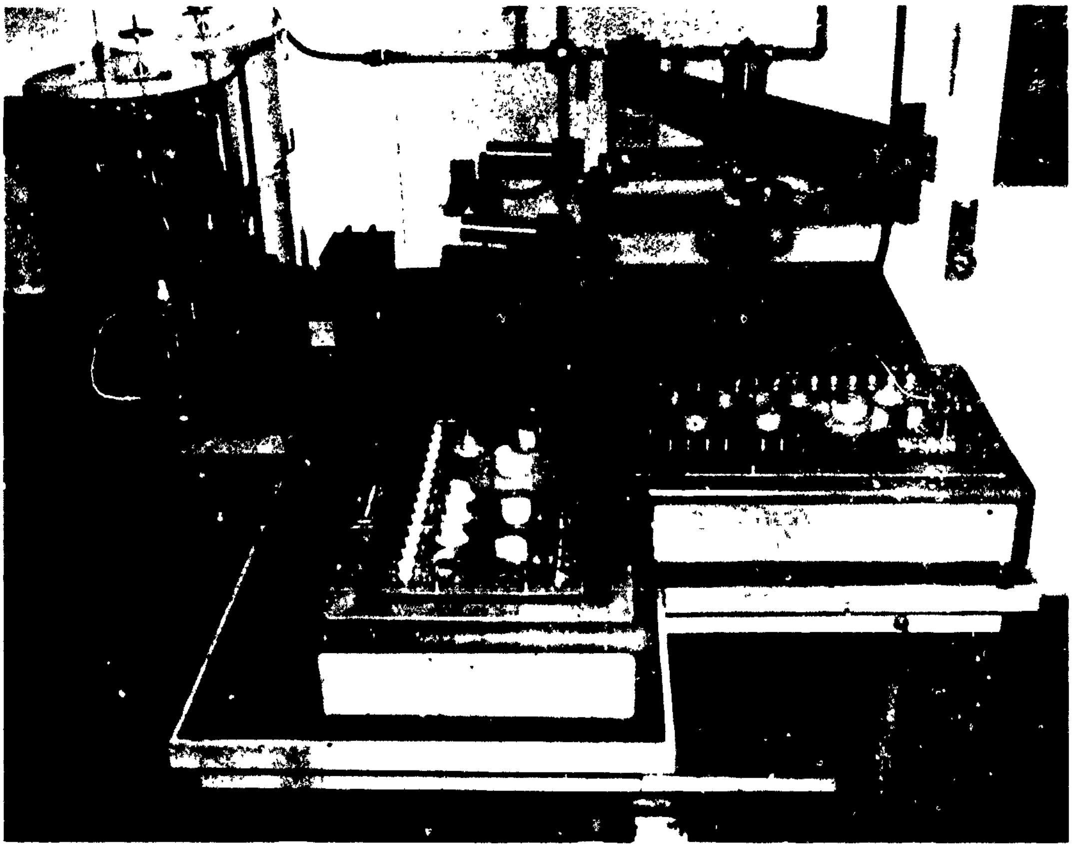

FIGURE 4. CALIBRATION EQUIPMENT FOR COMPARISON METHOD

1300°C in air and commercial hydrogen, and then re-calibrated in order to determine the effects of these operating conditions on the stability of the Platinel 2 couple.

B. Equipment

A Leeds and Northrup No. 8690 Millivolt Potentiometer was used to make the daily monitoring checks on the couples. The furnace was a platinum-wound tube furnace. Figure 3 is a schematic of the calibration equipment and Figure 4 is a photograph of this equipment.

C. Experimental Method

Fifteen matched couples (.020" dia. wire) were calibrated from 400 to 1300°C at 100°C intervals using a calibration procedure similar to that described in Reference 12. Calibration by Comparison Methods, page 9. See Appendix I for a description of the method. The standard thermocouple used in the calibration tests had been previously calibrated by the National Bureau of Standards. Sets of three couples, each from a different melt, were placed at varying depths of immersion into the platinum-wound tube furnace; one set of three couples was used to measure each of the five test temperatures, i.e., 600, 800, 1000, 1200 and 1300°C. The atmosphere was stagnant air or free-flowing hydrogen. Daily monitoring checks were made with the potentiometer to determine if the couples were stable. After approximately 1000 hours, the tests were stopped and the couples were re-calibrated. The actual times are given in the results.

D. Results

1. Tests in Air

The results of the life testing in air are shown below. These values are the aggregate drift from maximum positive to maximum negative occurring after 1100 hours.

Table No. 1

EMF Drift in Microvolts of 15 Platinel 2 Thermocouples from Three Lots Tested in Still Air

Calibration Temperature °C	Aging Temperature, °C 1300	1200	1000	800	600
	Change in Microvolts				
400	-40 to -130	140 to -20	70 to -10	120 to -20	40 to 130
500	-10 to -170	60 to -110	110 to 90	140 to -120	90 to 290
600	-60 to -170	10 to -150	150 to -110	100 to -80	[illegible]0 to [illegible]30

Table No. 1 - (Cont'd.)

EMF Drift in Microvolts of 15 Platinel 2 Thermocouples from Three Lots Tested in Still Air

Calibration Temperature °C	Aging Temperature, °C 1300	1200	1000	800	600
	Change in Microvolts				
700	50 to -160	50 to -60	140 to -50	210 to -30	60 to 80
800	80 to -110	90 to -20	100 to -50	120 to -40	-20 to 90
900	20 to -80	0 to -70	70 to -80	120 to -20	-60 to 90
1000	50 to -70	10 to -70	70 to -110	370 to -40	-60 to 10
1100	40 to -50	0 to -70	30 to -170	10 to -70	-10 to -40
1200	60 to -10	-20 to -130	0 to -150	-10 to -80	70 to -80

2. Tests in Hydrogen

Fifteen Platinel couples were tested in hydrogen - three at each of the following temperatures: 600, 800, 1000, 1200 and 1300°C. Of the couples tested at 1300°C, one failed completely after 216 hours, the second after 288 hours, while the third lasted 312 hours. Spot checks during this run indicated that the emf was stable.

A typical analysis of the hydrogen gas used in the test is as follows:

2 ppm oxygen
5 ppm carbon monoxide
20 ppm total hydrocarbon gas

A furnace failure during the hydrogen testing made it necessary to remove the bundle of thermocouples, and this caused failure by handling of one couple at each of 600 and 1200°C. The remaining ten couples successfully completed the 1000 hours at their respective temperatures. One of the three couples "dwelling" at 1000°C was removed after 500 hours to be re-calibrated and replaced to complete the 1000 hour test. The results of this re-calibration are shown in Table No. 2.

Table No. 2

Changes in Calibration of Platinel 2
Couple after 500 hours at 1000°C in
an Atmosphere of Commercial Hydrogen

Temp. °C	Original Calibration Millivolts	MV Comparison after 500 hours	μV
400	15.78	15.63	-150
500	20.34	20.14	-200
600	24.76	24.68	-80
700	29.25	29.14	-130
800	33.61	33.46	-150
900	37.74	37.64	-100
1000	41.69	41.63	-60
1100	45.47	45.42	-50
1200	49.06	49.00	-60

Of the original 15 couples, only ten were re-calibrated at the end of the test due to failure for the reasons mentioned earlier. The following table contains the calibration data and net change for these ten.

Table No. 3

Changes in Calibration of Platinel 2 Couples in Microvolts
After 1000 Hours at Various Temperatures
in an Atmosphere of Commercial Hydrogen

Re-Calibration Temp. °C	1	2	3	4	5	6	7	8	9*	10
	Aging Temp. 600°C		Aging Temp. 800°C			Aging Temp. 1000°C			Aging Temp. 1200°C	
400	-10	+40	+112	-110	-46	-50	-10	-10	-10	+337
500	-40	+30	+ 80	-70	-119	+ 0	-40	-20	-70	-491
600	+ 50	-10	+ 55	-30	-125	80	-10	-40	+ 50	-540
700	+ 20	+50	+ 65	-80	-146	0	+30	-80	-140	-433
800	+ 30	+30	+ 63	-100	-10	+10	-20	-80	-150	-428
900	+110	+20	+ 70	-130	+ 4	-90	0	-60	+210	-450
1000	+ 90	+20	+ 75	-120	+31	-90	-20	-10	+160	-445
1100	+ 90	+40	+ 49	-130	+ 9	-90	-10	-90	-170	-453
1200	+ 80	+40	+ 61	-120	-11	-80	-40	-120	+150	-541

* Thermocouples 4 and 9 were re-annealed before re-calibration.

At this point, it was felt that additional tests in hydrogen at 1200°C and 1300°C were warranted. However, the two additional tests at 1300°C failed; one at the end of 360 hours and the other at the end of 431 hours. Of the 2 additional couples aged at 1200°C, one failed after 508 hours; the second was re-calibrated at this time, and the results are shown in Table No. 4. This latter couple was again introduced

into the furnace at 1200°C and aging continued in hydrogen. It ultimately failed after a total of 892 hours.

Table No. 4

Changes in Calibration of a Platinel 2 Couple After 508 Hours at 1200°C in an Atmosphere of Commercial Hydrogen

Re-Calibration Temp., °C	Initial Calibration, MV	Calibration at 508 Hrs., MV	Drift, V
400	15.85	15.49	-360
500	20.36	20.03	-330
600	24.88	24.56	-320
700	29.33	29.11	-220
800	33.70	33.51	-190
900	37.83	37.65	-180
1000	41.77	41.70	-70
1100	45.56	45.48	-80
1200	49.14	49.12	-20
1300	52.47	52.49	+20

E. Interpretation of Results

1. Tests in Hydrogen at 1200°C and 1300°C

All five couples tested at 1300°C failed before the completion of the tests. The times for failure are 216, 288, 312, 360 and 431 hours. It appears, on the basis of five tests, that the life of Platinel 2 for continuous use, in an atmosphere of free-flowing hydrogen at 1300°C, is, for most cases, somewhere between 200 and 400 hours.

Of the four couples tested at 1200°C, two completed a life test of 1000 hours; these results were reported in Table No. 3. The two remaining couples each failed prematurely; one at 508 hours, the other at 892 hours.

2. The Method of Failure of Platinel 2 Thermocouples Aged in Commercial Hydrogen for Long Periods of Time

In every instance wherein the test of a Platinel 2 couple was not purposely terminated at the end of an aging period of 1000 hours, the evidence in this series of runs substantively shows several coincident facts regarding the method of failure. Invariably, it is the negative (1503, 65 Au - 35 Pd) component - M.P. equals 1426°C - which is responsible for the ultimate

failure of the couple. Below the aging temperature of 1000°C, none of the test couples failed within the 1000-hour life test, as occurred at the 1200 and 1300°C levels.

Incipient failure is caused by progressive and uniform volatilization of the negative component. This condition is shown in Figure 5 wherein the negative component is to the right and has been reduced to approximately 50% of its original 20 mil diameter. Beads of deposited metal are in evidence on the face of the insulator. This was the condition of a Platinel 2 couple after aging for 508 hours at 1200°C in an atmosphere of commercial hydrogen.

Figure 6 is a photograph of the same couple after 892 hours of test, and shows complete failure; the positive component - to the left - has undergone negligible reduction of size.

In contrast to this latter couple, Figure 7 represents a Platinel 2 couple aged at 800°C for 508 hours in hydrogen. Again the negative element - to the right - indicates a reduction of size but to a much less degree than the previous couple. In this case, there is a complete absence of metal deposition.

Figure 8 shows an enlarged view of a section of the negative component removed from within the insulator. Here the metal deposition has been restricted by the wall of the insulator bore and has formed a veil-like protrusion along the body of the wire.

Figure 8 also indicates the method by which the negative component ultimately fails. This figure shows six contiguous segments joined at grain boundaries of reduced sections.

Prolonged heating of this wire has both reduced its diameter and has lowered the melting point of the grain boundary constituent. The ultimate failure is caused by intergranular melting while the wire is still of substantial size (50% or less).

Although micro-examination has revealed the mechanism of failure, the metallurgical reasons remain unknown.

Figure 9 represents a longitudinal section of the negative component of a Platinel 2 couple aged at 1200°C for approximately 900 hours in hydrogen. The upper end of the photograph represents an area approximately 1/8" from the bead, while the bottom of the photograph

Figure 5

View Showing Partial Failure of Beaded Junction

Negative component of Platinel 2 thermoelement - to the right - reduced 50% after aging 508 hrs. in hydrogen at 1200°C.

Mag. 15X

Figure 6

Complete failure of negative component after 892 hrs in hydrogen at 1200°C.

Mag. 15X

Figure 7. Platinel Couple After Aging in Hydrogen at 800°C for 503 hrs.

Mag. 15X

Figure 8. Negative Component of Platinel Undergoing Incipient Failure

Mag. 40X

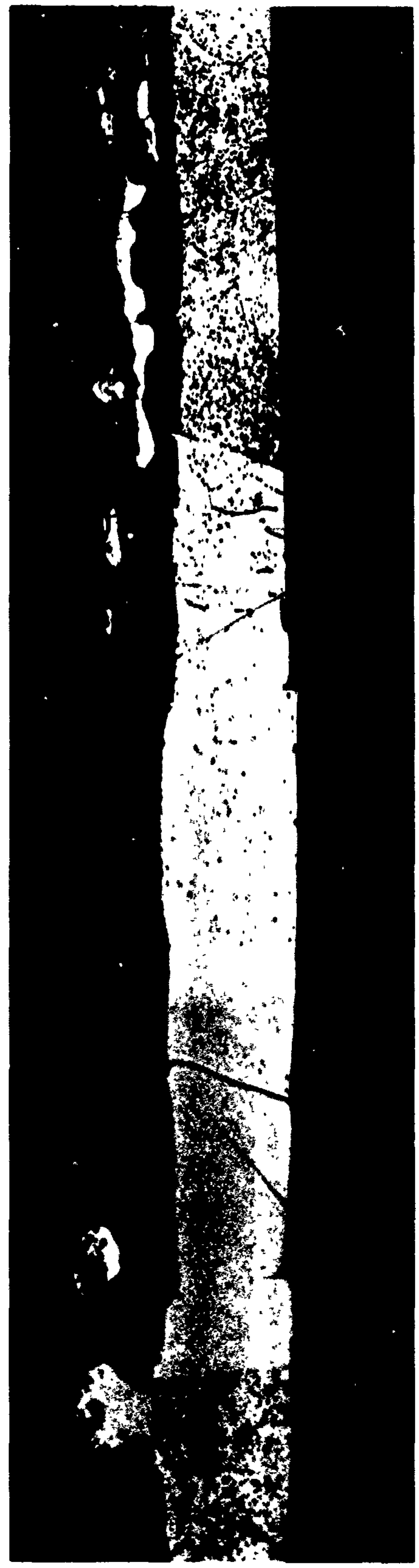

Figure 9

Longitudinal Section of Platinel 2
Negative Component

Note etch pits along various crystallographic planes. Aged at 1200°C for approximately 900 hours in hydrogen.

Mag. 75X

Figure 10

Photomicrograph of Platinel 2
Negative Leg

Figure 11

Photomicrograph of Platinel 2
Negative Leg

Figure 12

Photomicrograph of Platinel 2
Negative Leg

The configuration of several etch pits in Platinel 2 negative component associated with varying crystallographic planes. Aged at 1200°C for approximately 900 hours in hydrogen

Mag. 1500X

shows an area 1/2" from the bead. To the left of the section are the remains of a veil and volatilized beads, previously referred to, entrapped by the insulator wall. Inasmuch as there have been queries in the past regarding what appears to be a second phase or a precipitate in some of the grains, this photomicrograph is included merely to dispel such reasoning.

At higher magnification (1500X) it becomes evident that what appears to be a second phase is in reality the etching effect on different crystallographic planes. Figures 10, 11 and 12 illustrate this point.

F. Conclusions and Recommendations

Calibration results of Platinel 2 aged in commercial hydrogen for 1000 hours at temperatures up to 1000°C show good stability in that at no time did the drift exceed ±3/4% allowed between 350 and 1260°C for base-metal type thermocouple material.

However, there is a disparity in the results reported for the couples aged at 1200°C in that of two similarly aged couples, one endured almost twice as long as the second (892 hours vs. 508 hours).

Also, the drift in one of the couples which endured the 1000-hour test was much larger than the other.

Additional tests at 1200°C in hydrogen appear to be warranted.

1 (c). Resistivities of Individual Legs of Platinel 2 Thermocouple

A. Objective

Three samples each of three different melts of 1503 and 1813 were tested to determine the average resistivity of each leg at temperatures from 0° to 1200°C.

B. Equipment

The equipment for this task consisted of a Honeywell Mueller Bridge, Leeds and Northrup No. 2285-B galvanometer, Leeds and Northrup galvanometer scale, Keithley 150-A microvolt-ammeter, platinum wound muffle furnace (with platinum ground tube) calibrated Pt vs. Pt10Rh thermocouples, and a Leeds and Northrup No. 8690 portable potentiometer. A voltage stabilizer and a powerstat were used to heat the furnace to a stable temperature which was then measured with the potentiometer. Figure 14 shows the test

set-up, Figure 15 is a photograph of the test specimen, and Figure 13 is a schematic of the test equipment.

C. Experimental Method

Each specimen to be tested was non-inductively wound on a pure alumina grooved tube. The temperature in the furnace was first measured with the Pt vs. Pt10Rh thermocouple using the potentiometer, and then the resistance was measured with the Mueller Bridge.

Due to the sensitivity of the instruments used, all were grounded to a common post. A ground shield tube around the specimen was necessary to prevent "pick-up" due to induction from the furnace windings. A transite box covered the furnace to prevent the temperature from changing due to air circulation. A series of variable resistors was used to vary the current to the specimen and the Mueller bridge. 0.6 milliamps were used to inhibit self-heating, and gave a satisfactory result. The specimen was 0.005" in diameter and 42 ±1/2" long.

D. Results

Table No. 5 gives the average resistivity values vs. temperature rounded-off to the nearest ohm.

Figure 16 contains the same data plotted on a graph.

Table No. 5

Average Resistivities of Platinel 2
(For Each Leg Sample From Three Different Bars)

Resistivity, Ohms per Circular-MIL Foot

Temp., °C	Alloy 1813	Alloy 1503
0	184	144
50	192	147
100	200	150
150	208	153
200	216	156
250	224	158
300	232	160
350	240	162
400	247	164
450	254	166
500	261	168
550	267	170

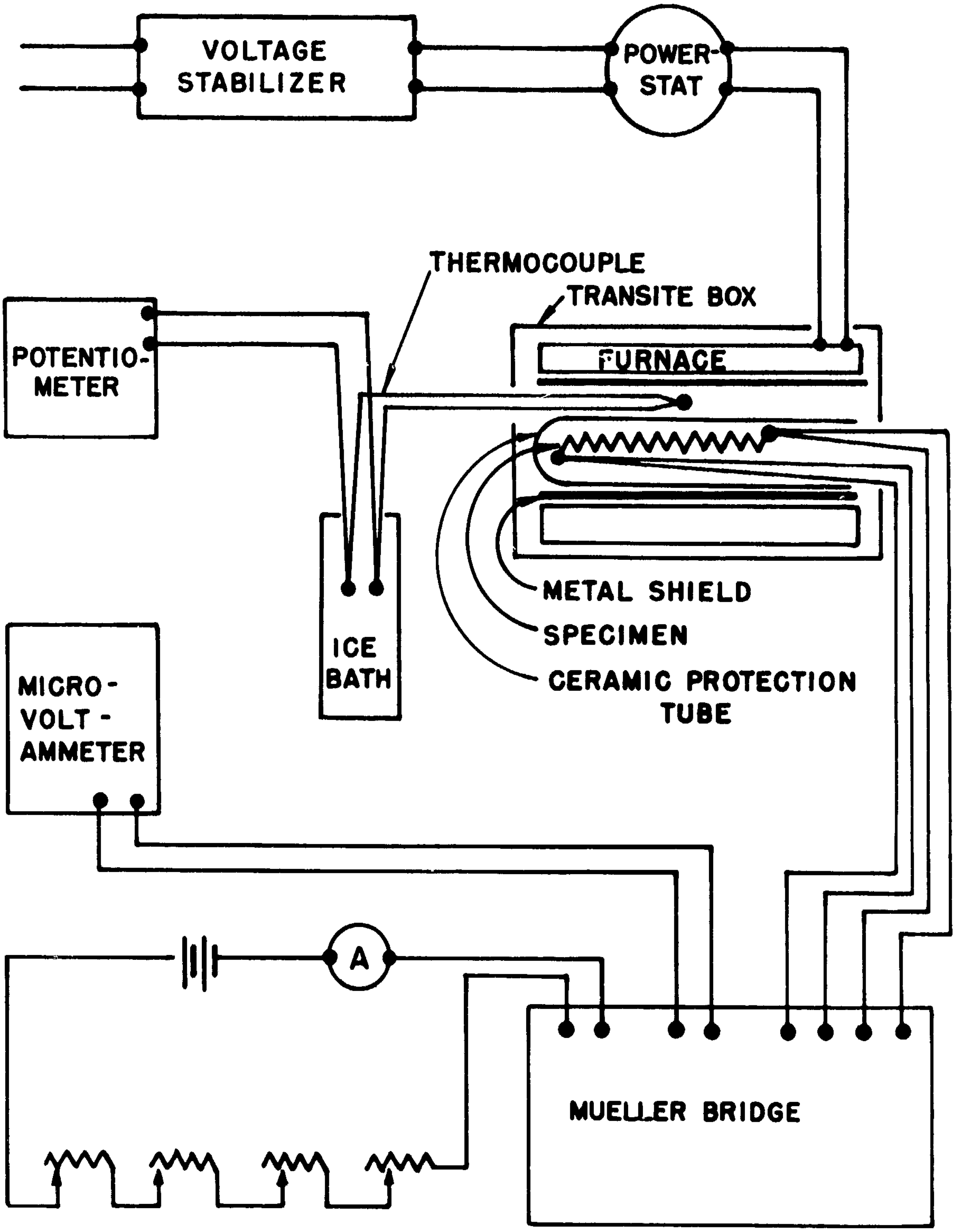

Figure 13. Schematic of Resistivity Test Equipment

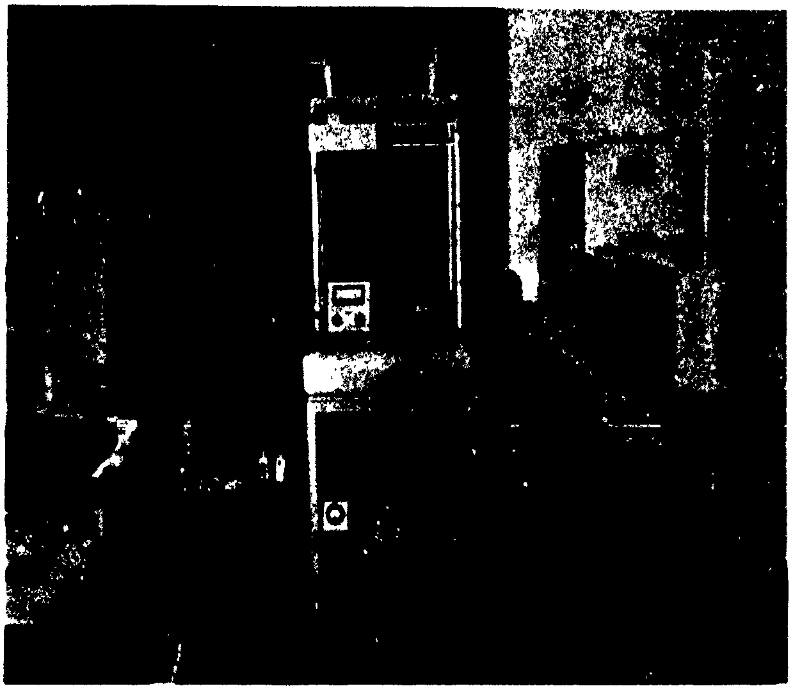

FIGURE 14. TEST STAND

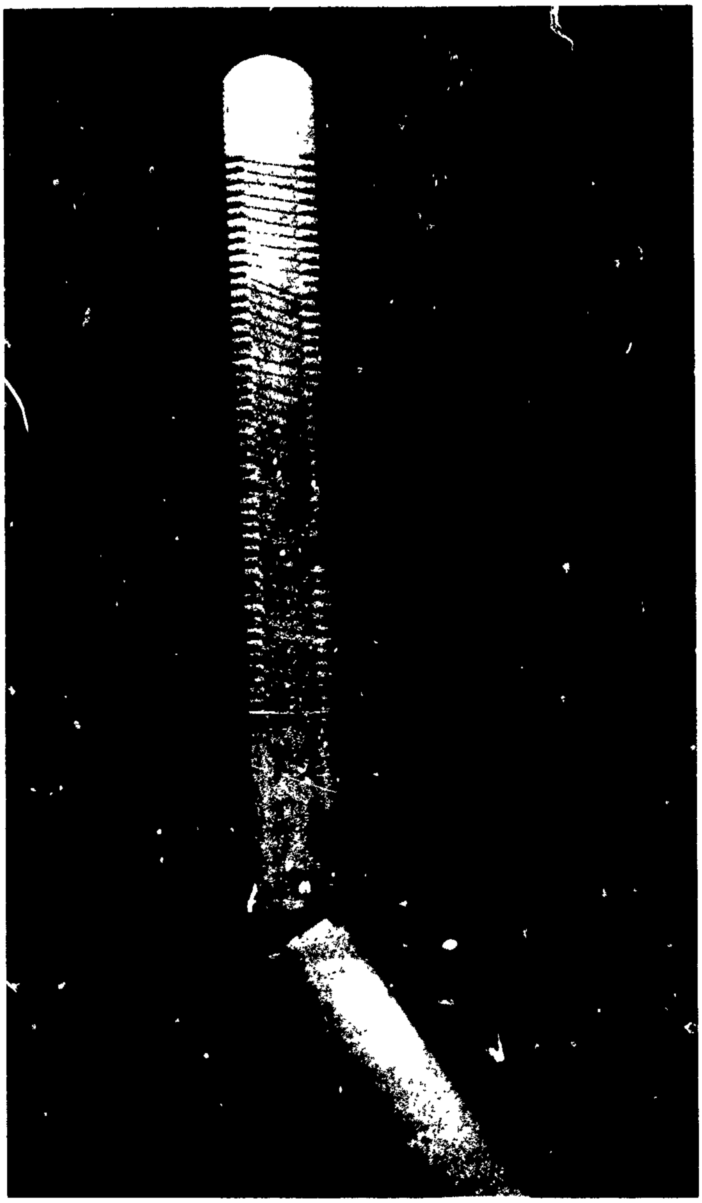

Figure 15. Resistivity Test Specimen

Mag. 2X

FIGURE 16

RESISTIVITY OF PLATINEL 2

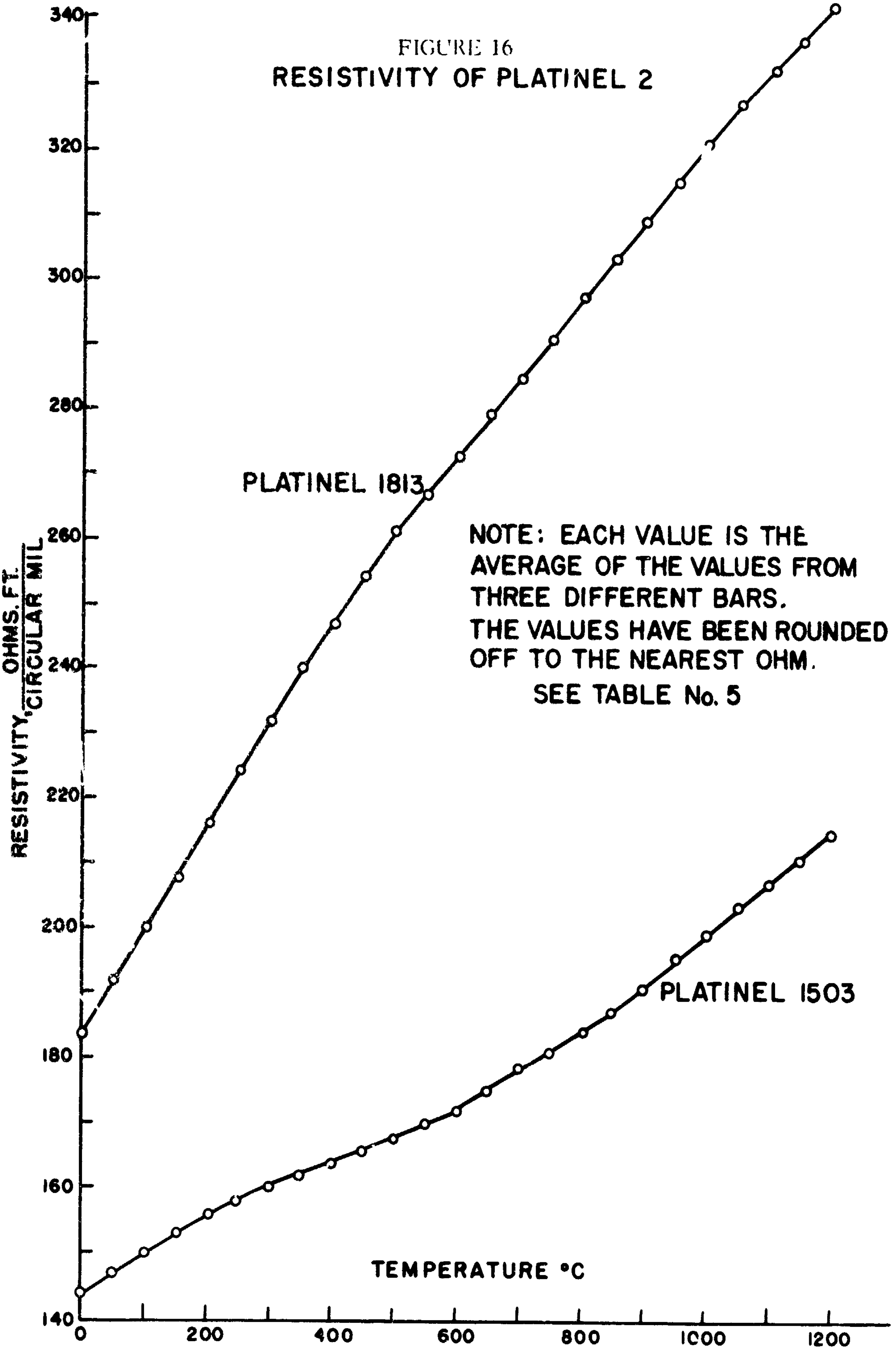

Table No. 5 - (Cont'd.)

Temp., °C	Alloy 1813	Alloy 1503
600	273	172
650	279	175
700	285	178
750	291	181
800	297	184
850	303	187
900	309	191
950	315	195
1000	321	199
1050	327	203
1100	332	207
1150	337	211
1200	342	215

E. Interpretation of Results

It can be seen from Figure 16 that, within the temperature range of testing, the resistivity of Platinel 1813 is higher than that of Platinel 1503.

1 (d). Mechanical Properties at High Temperature

A. Objective

To perform tensile and stress-to-rupture tests on Chromel, Alumel, 1503, 1813, Fibro 1503, Fibro 1813, Palladium, Fibro Palladium and Platinum-15% Iridium at 800, 1000, and 1200°C.

B. Equipment

Equipment required includes tube furnaces, Dillon Tensile Testing Machine for hot tensile tests, constant voltage transformers to insure constant temperature during stress-to-rupture tests, and a Leeds and Northrup Multi-Point Recorder.

The stress- -rupture testing of the metals and alloys tested in t is program was performed on equipment shown in schemati drawing, Figure 17. Figure 18 is a photograph of the stress-to-rupture furnaces. The hot tensile testing was conducted in a manner similar to that for the stress-to-rupture tests except that the tension in the wire was applied by a Dillon tensile testing machine. Figure 19 is a photograph of this equipment.

C. Experimental Method

1. Hot Tensile Testing

The accuracy of the Dillon tensile tester was checked against a Baldwin-Southwark tensile tester and an Instron tensile tester; in either case the error was less than 3%.

The wire specimens were 22" in length and 0.050" in diameter. The specimens were marked with ferric chloride which turns black when it is heated, and this coloring enabled the elongation to be measured. The specimens were heated for five minutes and then extended at a rate of 0.5" per minute which is above the A.S.T.M. standard of 0.2" per minute.

2. Stress-to-Rupture Testing

The specimens were annealed while they were at 0.100" diameter and then worked down to 0.050" diameter without further annealing. The specimens used were 17" in length and 0.050" in diameter. The furnace was 12" long and had a 5" uniform heat zone. A thermocouple to the center of the furnace gave continuous readings of furnace temperature. When the specimen failed, the weight hit the microswitch, stopping the timer. The specimen fracture had to occur within the heat zone in order for the test to be valid, i.e., tests were run until at least three fractures occurred within the heat zone.

D. Results

Stress-to-rupture testing of Chromel and Alumel was discontinued after some tests were run at 1200°C. Data obtained at this temperature were spotty and it was not possible to interpret them. Since it was expected that the problem would be more difficult at the lower temperatures and that any interpretation which would be made would not be valid, it was decided not to test at the lower temperatures.

The following data are for Chromel.

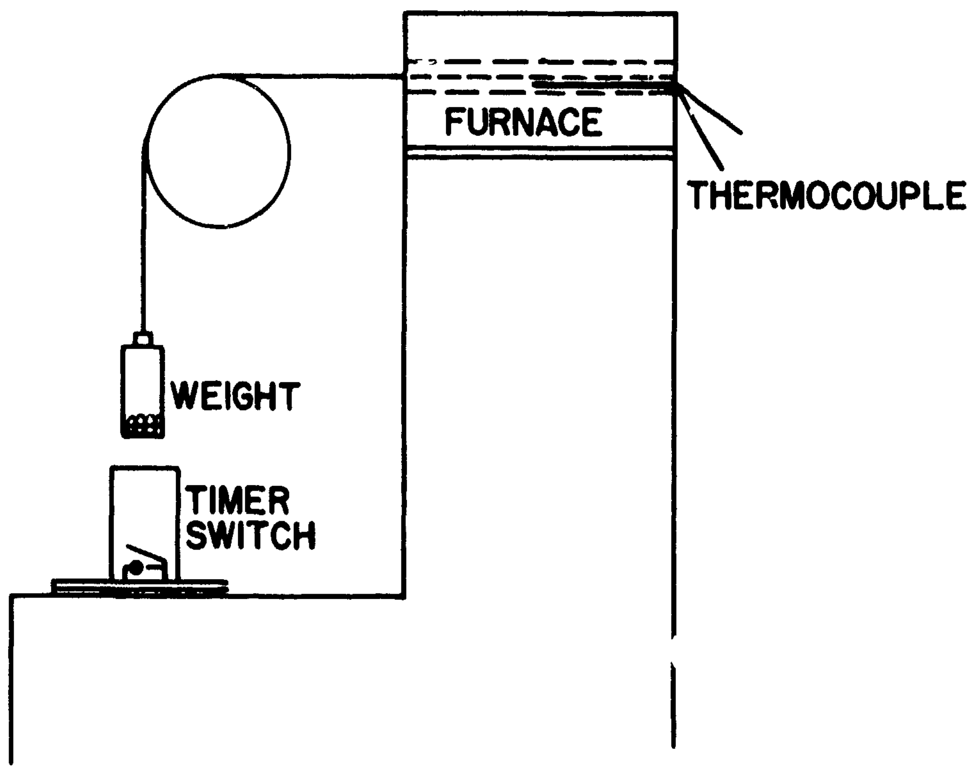

Figure 17. Schematic of Stress to Rupture Equipment

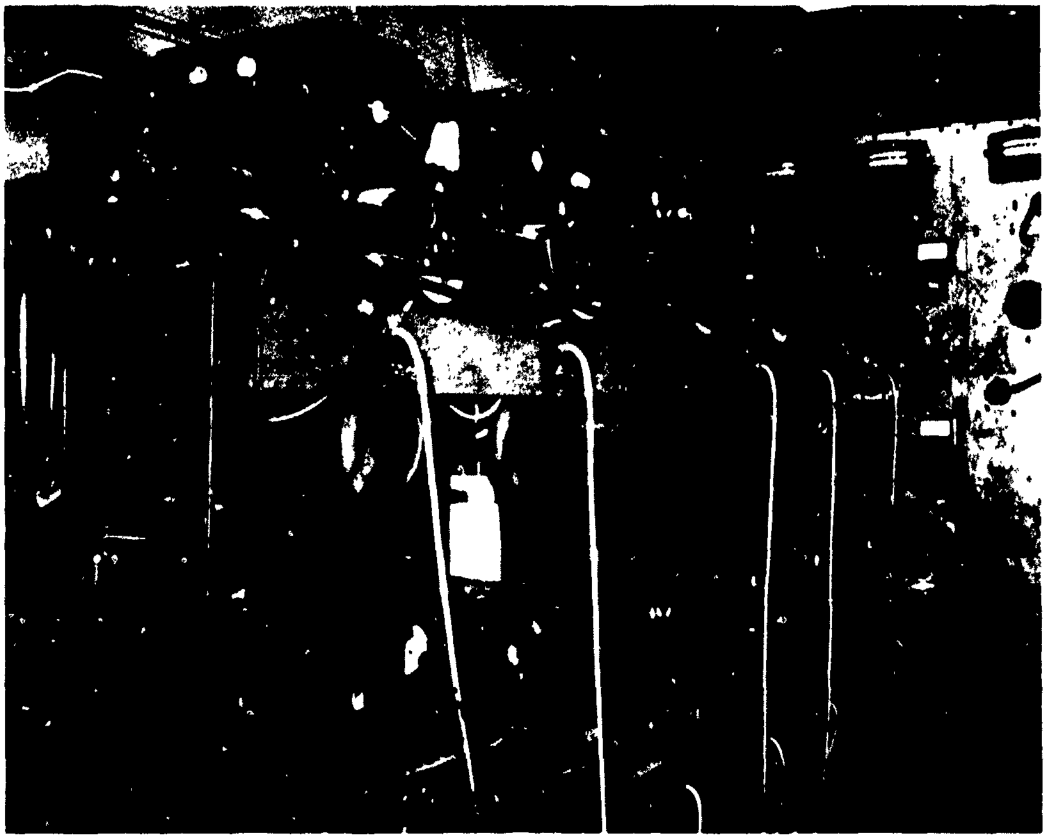

FIGURE 18. STRESS-TO-RUPTURE FURNACES

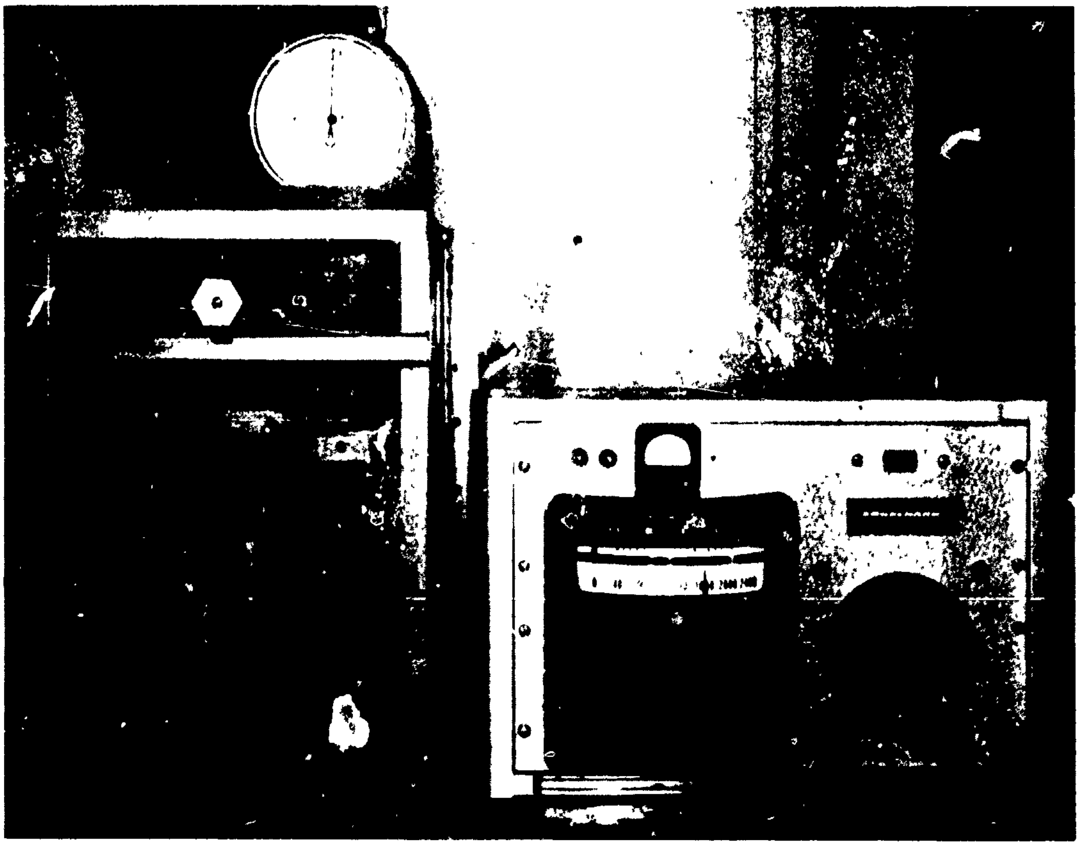

FIGURE 19. DILLON TENSILE TESTING MACHINE

Table No. 6

Stress-to-Rupture Test
For Chromel P Wire

Temp. °C	Load, Grams	Life, Hours
1200	700	Over 200 hours
1200	1200	Over 200 hours
1200	1600	Over 200 hours
1200	2000	2.4
1200	1800	10.0
1200	1800	9.5
1200	1800	7.1
1200	1700	Over 200 hours
1200	1700	Over 200 hours
1000	2250	80.7
1000	2250	600
1000	2700	59

It will be noted that at the 1000°C test temperature, two consecutive samples having the same load failed at diverse intervals. A definite pattern could not be determined. The problem with Alumel was quite similar.

Stress-to-rupture testing of Pt15%Ir was conducted at 1000 and 1200°C but was not done at 800°C since this material is beyond the capacity of the test equipment at this temperature.

Figures 20 to 23 inclusive illustrate the stress-to-rupture results.

Figures 24 to 29 inclusive illustrate the hot tensile results for the nine materials tested.

E. Interpretation of Results

Preliminary studies of the stress-to-rupture data indicate that there would be no advantage in using Fibro 1813 or Fibro 1503 instead of regular Platinel 2 alloys. A comparison of the two sets of curves shows no set pattern or trend. In the case of the 1813 alloy, there is a definite loss of rupture strength at the higher temperatures of 1000 and 1200°C, whereas in the 1503 alloy, there is virtually no difference in stress-to-rupture at these temperatures. Contrary to the results obtained with pure platinum, there appears to be no significant gain in rupture strength in Fibro palladium over regular palladium at 1200°C. At 800 and 1000°C, however, some worthwhile advantages may be noted.

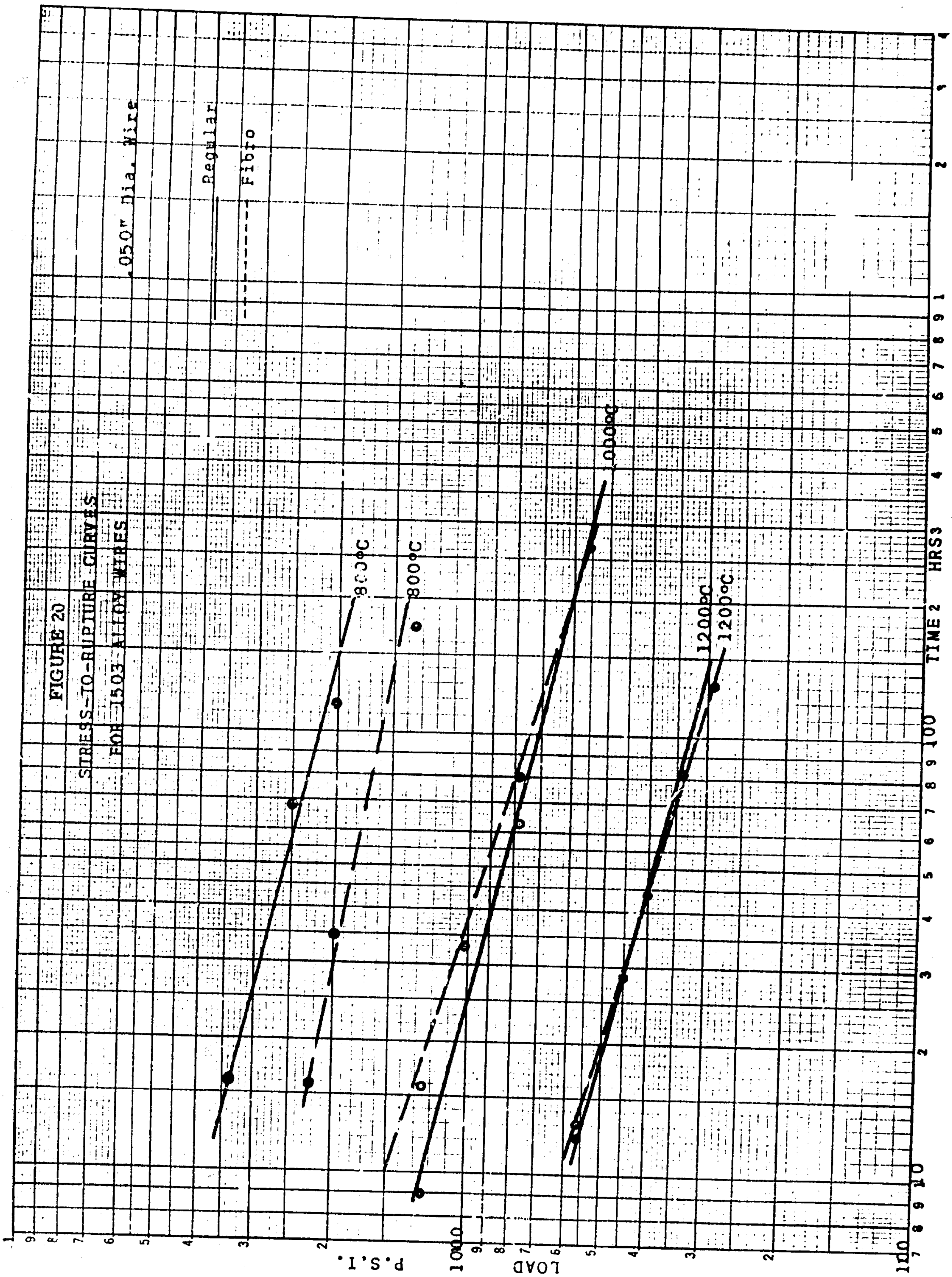
FIGURE 20
STRESS-TO-RUPTURE CURVES
FOR 1503 ALLOY WIRES
.050" Dia. Wire
Regular
Fibro
800°C
800°C
1000°C
1200°C
1200°C
TIME HRS
LOAD P.S.I.

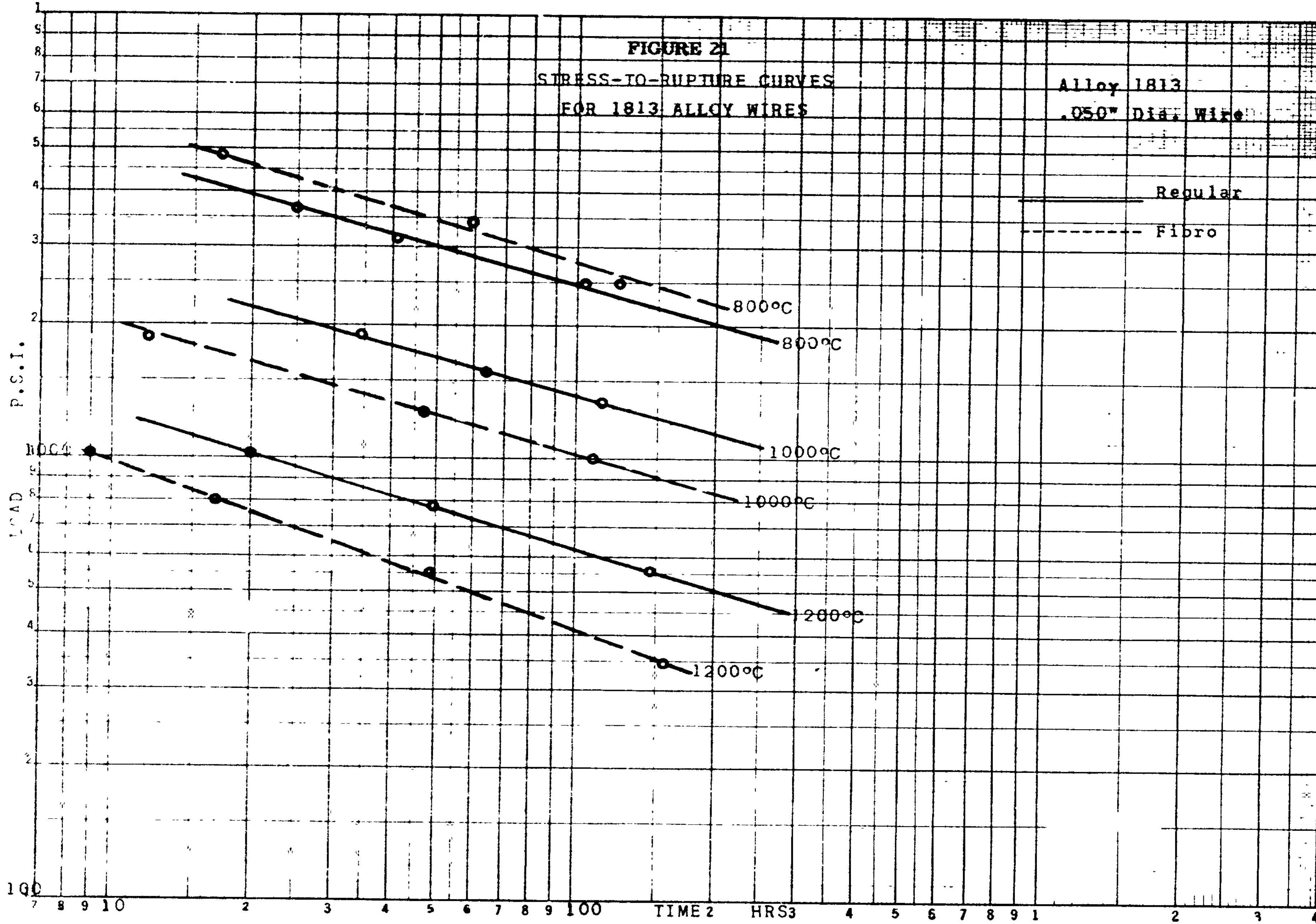

FIGURE 21

STRESS-TO-RUPTURE CURVES
FOR 1813 ALLOY WIRES

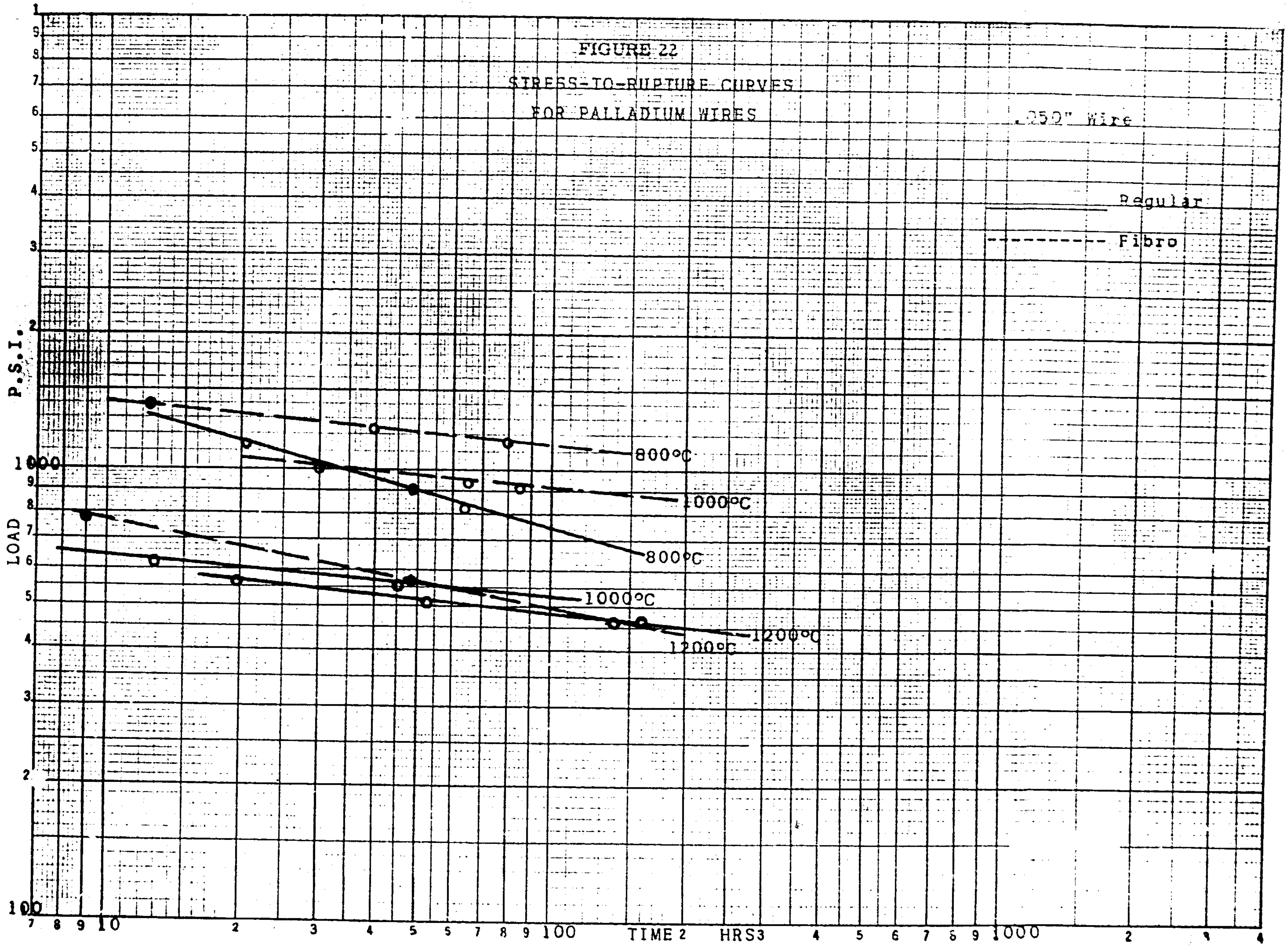
FIGURE 22
STRESS-TO-RUPTURE CURVES
FOR PALLADIUM WIRES
.050" Wire
Regular
Fibro
800°C
1000°C
800°C
1000°C
1200°C
1200°C
P.S.I.
LOAD
TIME HRS

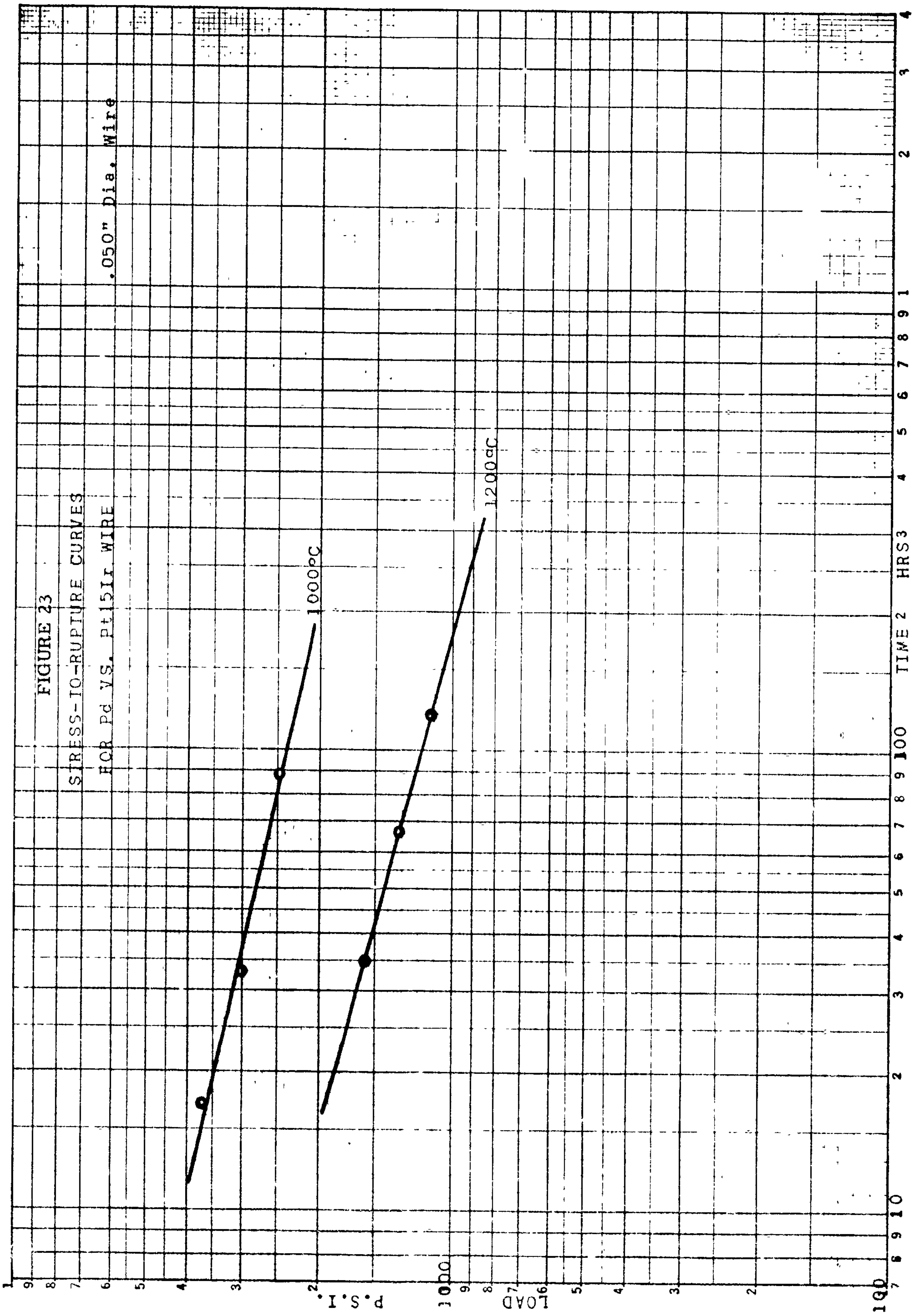
FIGURE 23
STRESS-TO-RUPTURE CURVES
FOR Pd VS. Pt15Ir WIRE
.050" Dia. Wire
1000°C
1200°C
LOAD P.S.I.
TIME HRS

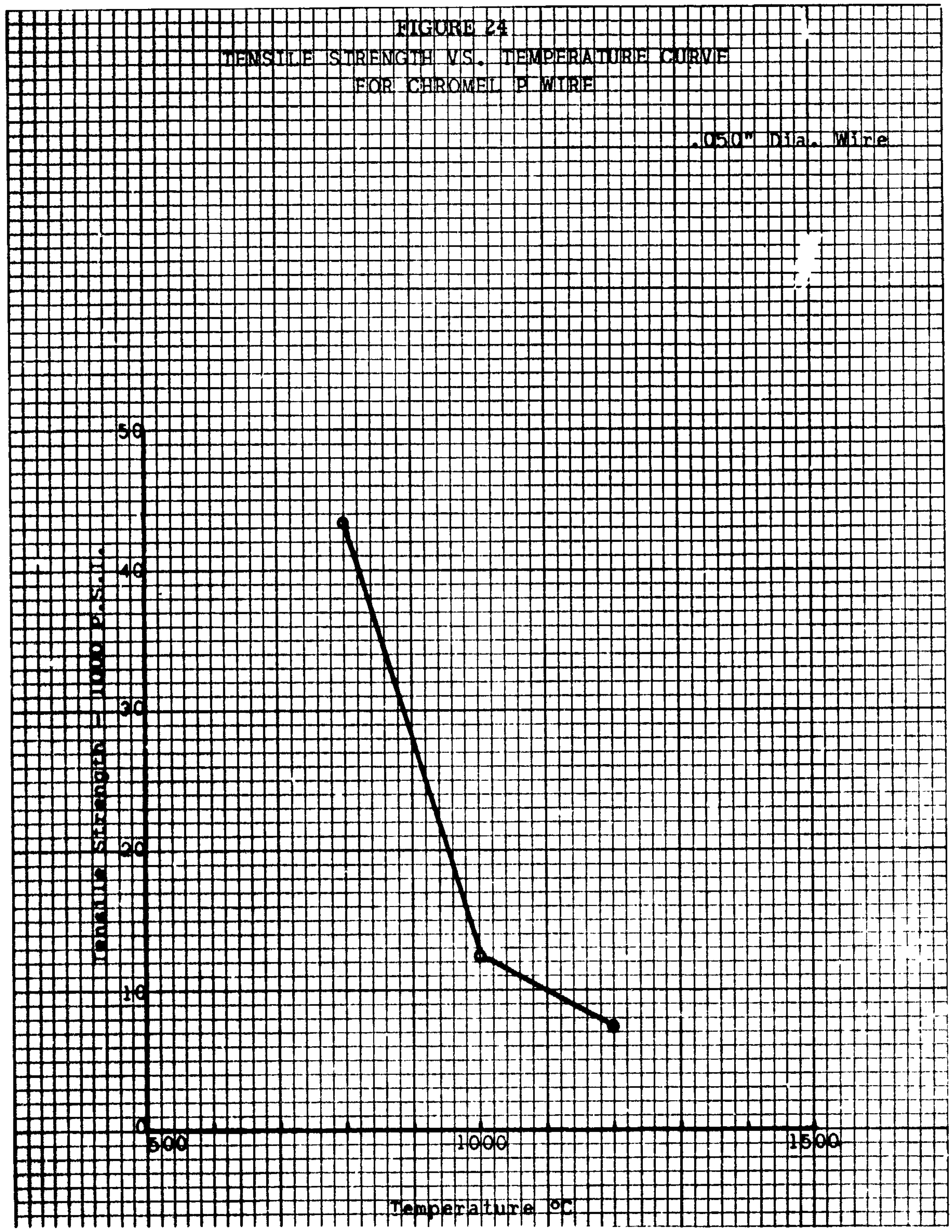
FIGURE 24
TENSILE STRENGTH VS. TEMPERATURE CURVE
FOR CHROMEL P WIRE
.050" Dia. Wire
Tensile Strength - 1000 P.S.I.
50
40
30
20
10
0
500
1000
1500
Temperature °C

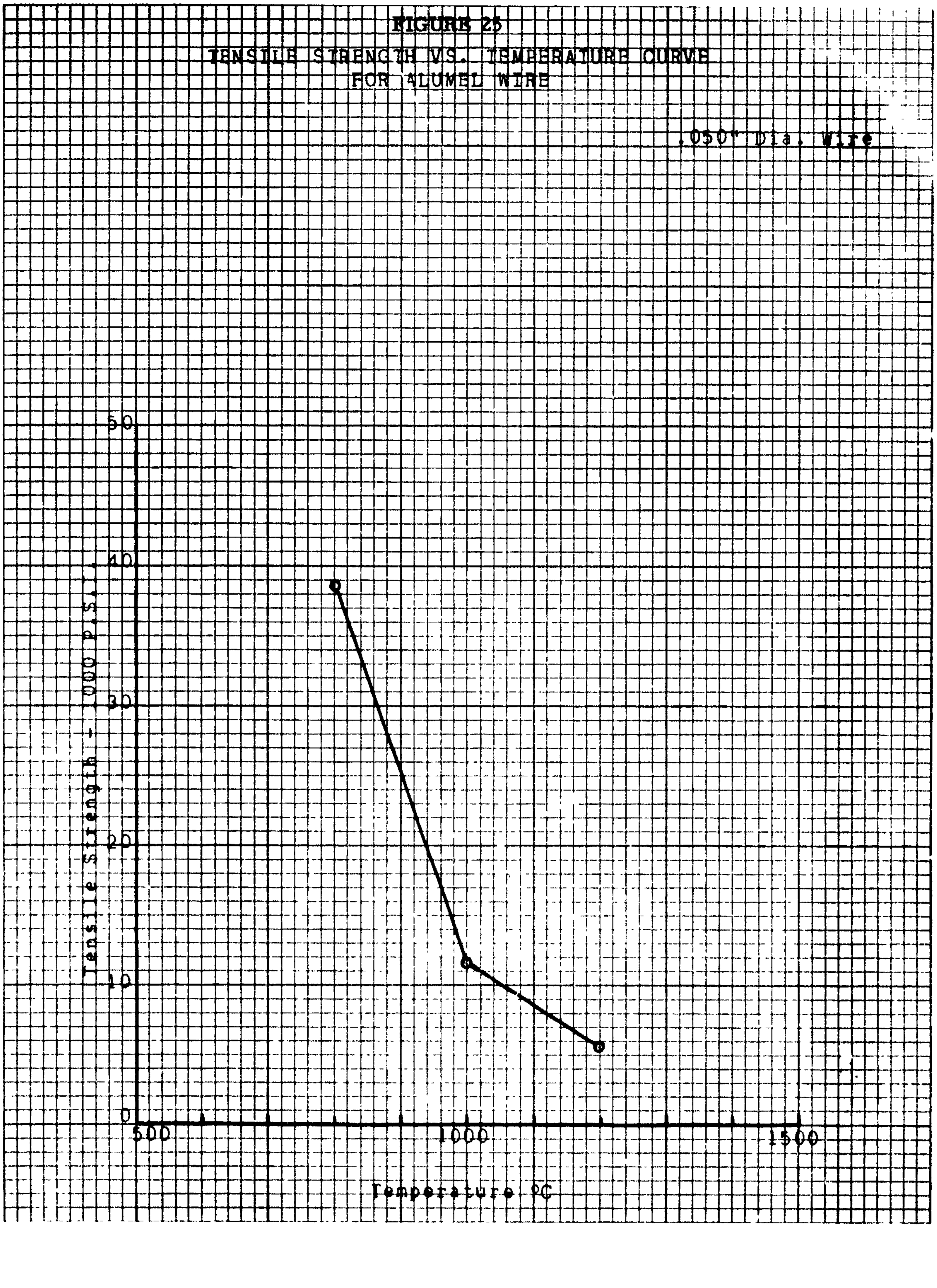
FIGURE 25
TENSILE STRENGTH VS. TEMPERATURE CURVE
FOR ALUMEL WIRE
.050" Dia. Wire
Tensile Strength - 1000 P.S.I.
50
40
30
20
10
0
500
1000
1500
Temperature °C

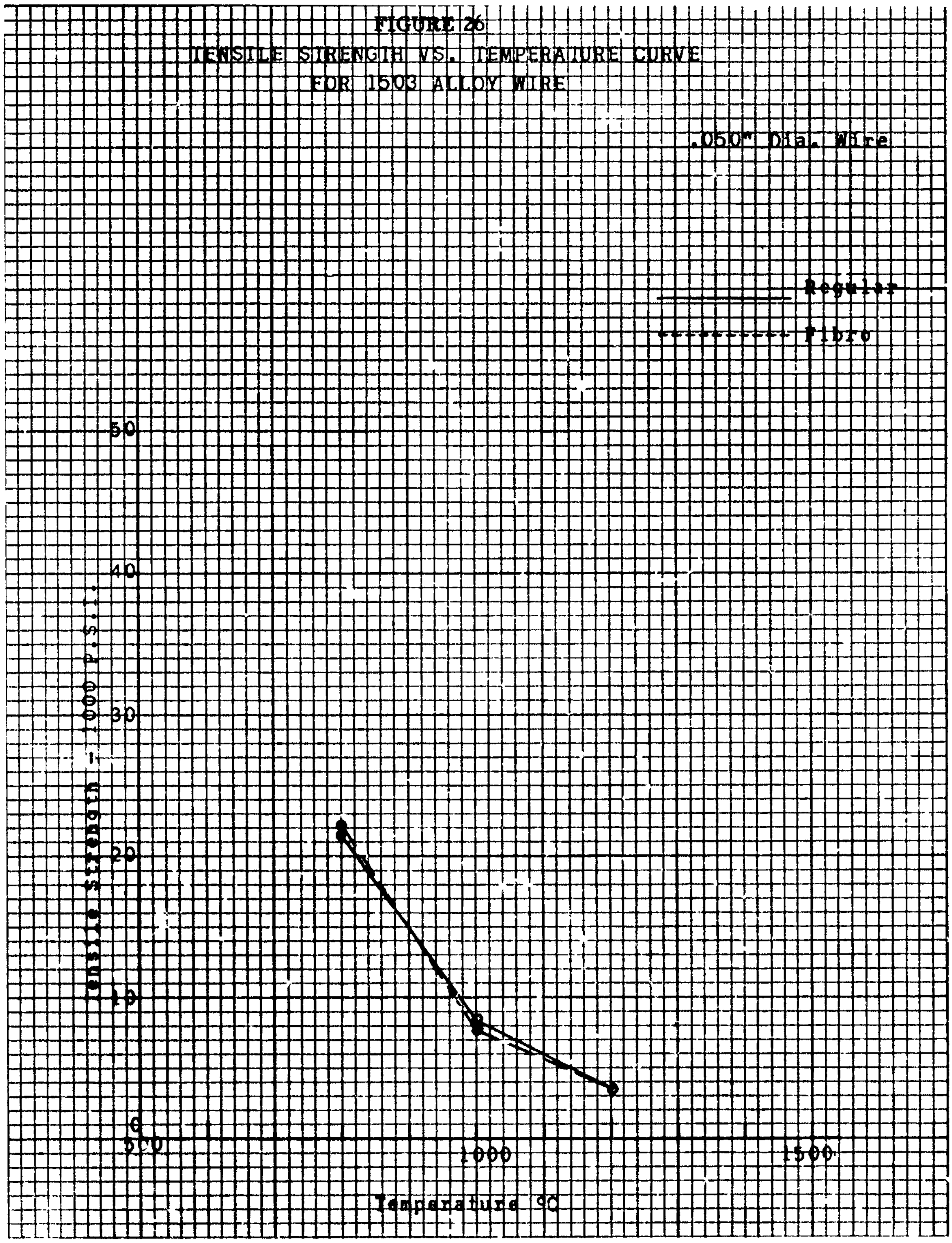
FIGURE 26
TENSILE STRENGTH VS. TEMPERATURE CURVE
FOR 1503 ALLOY WIRE
.050" Dia. Wire
Regular
Fibro
50
40
30
20
10
0
500
1000
1500
Tensile Strength - 1000 P.S.I.
Temperature °C

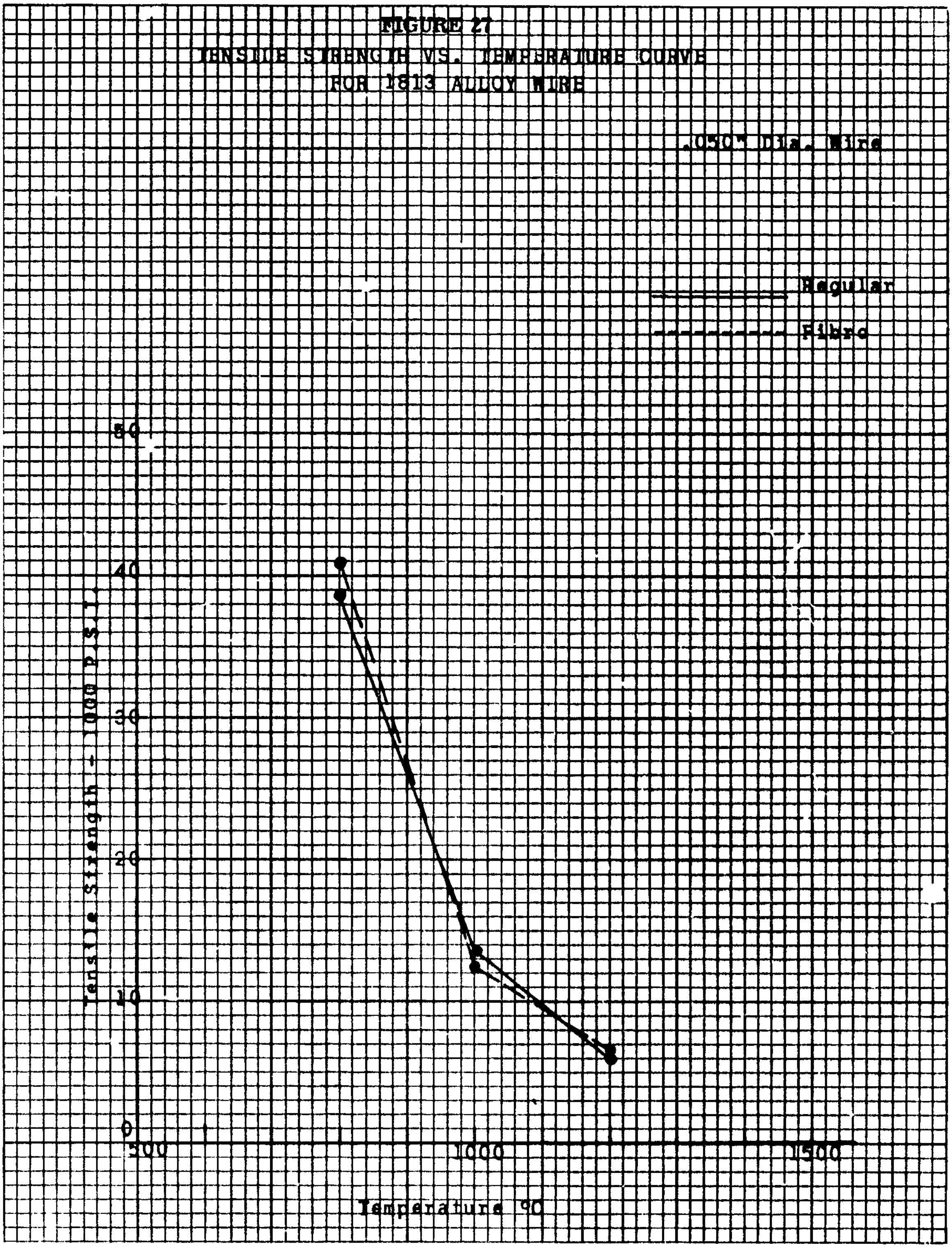
FIGURE 27
TENSILE STRENGTH VS. TEMPERATURE CURVE
FOR 1813 ALLOY WIRE
.050" Dia. Wire
Regular
Fibre
50
40
30
20
10
0
500
1000
1500
Tensile Strength - 1000 P.S.I.
Temperature °C

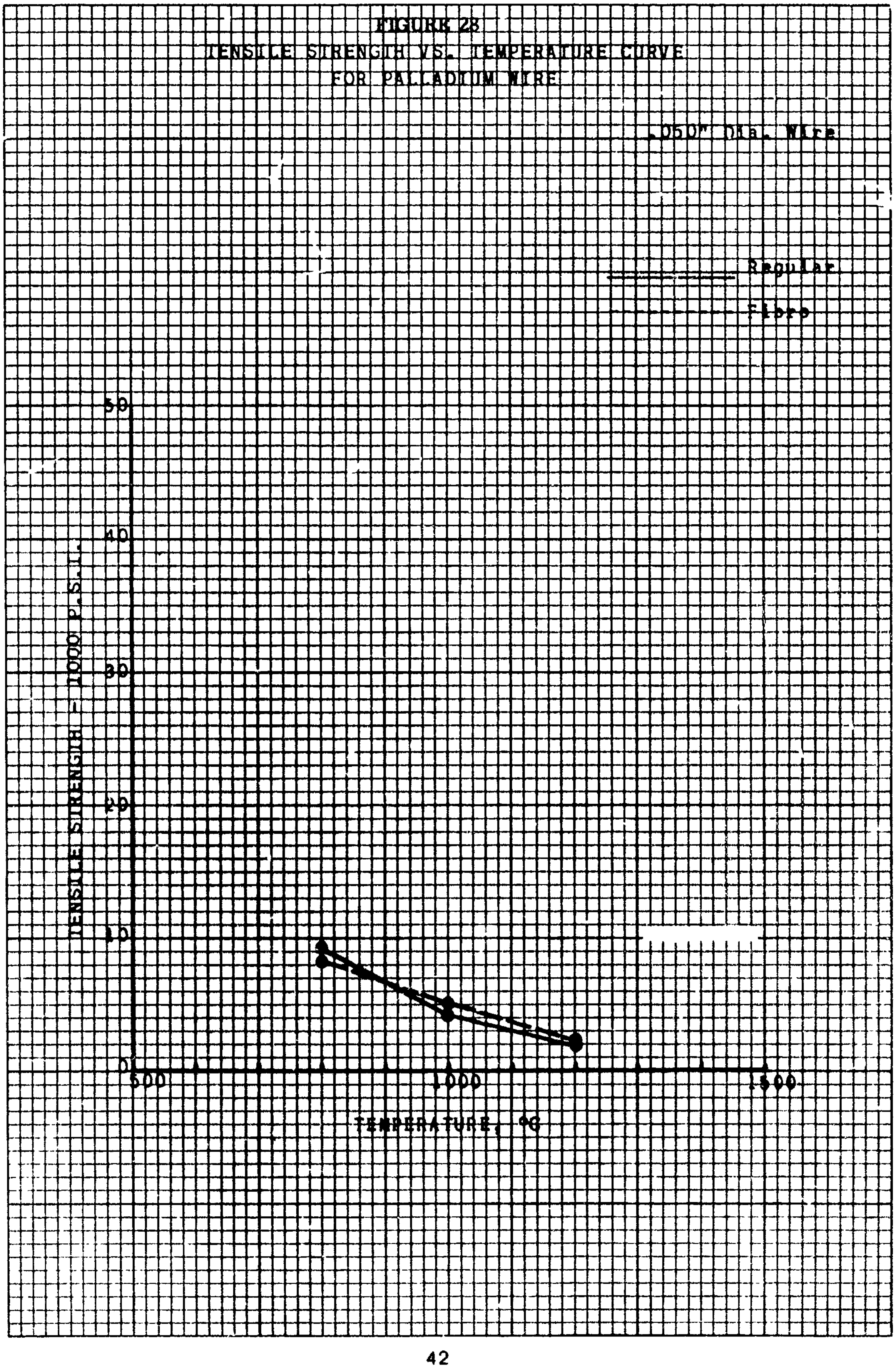
FIGURE 28
TENSILE STRENGTH VS. TEMPERATURE CURVE
FOR PALLADIUM WIRE
.050" Dia. Wire
Regular
Fibro
TENSILE STRENGTH - 1000 P.S.I.
50
40
30
20
10
0
500
1000
1500
TEMPERATURE, °C

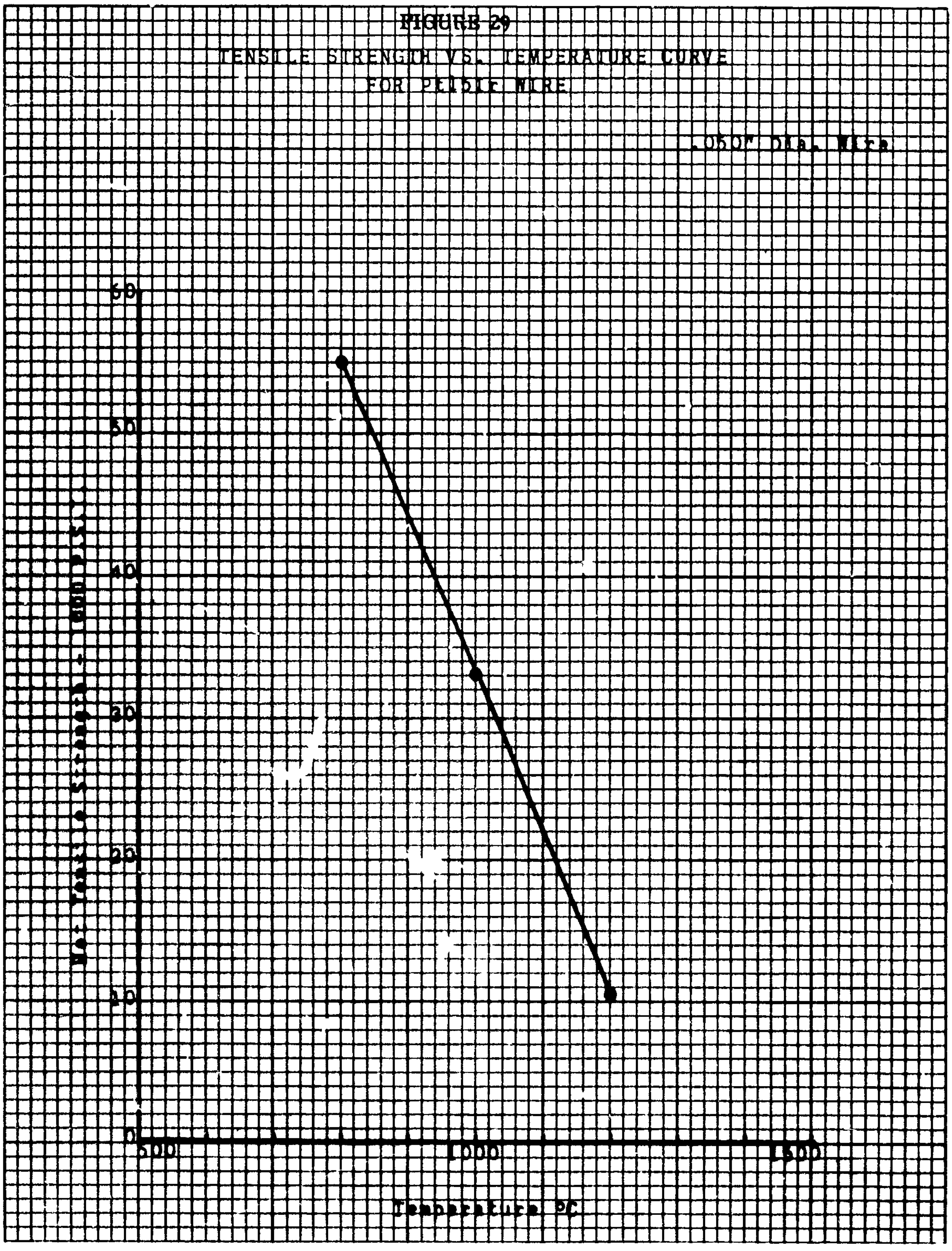

FIGURE 29

TENSILE STRENGTH VS. TEMPERATURE CURVE
FOR Pt15Ir WIRE

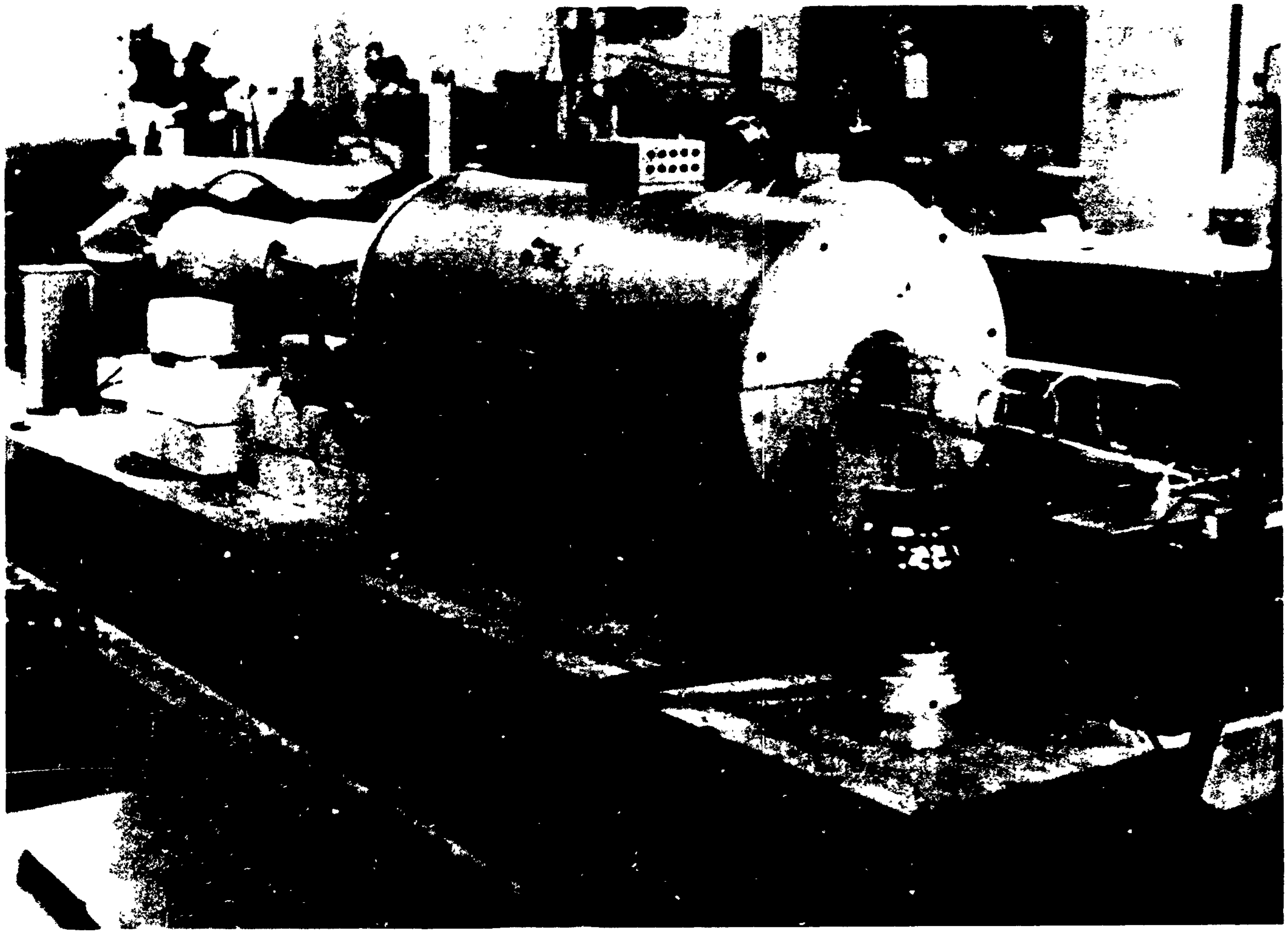

Figure 30. Test Setup

A study of the hot tensile test data from a thermocouple design viewpoint is interesting. A comparison of the relative strengths of the legs of the Pd. vs. Pt15%Ir couple at 1000°C, for example, reveals a tensile strength of 4000 psi for regular grade palladium as against 33.000 psi for the Pt15%Ir wire. Fibro palladium at the same temperature has approximately 25% greater strength or 5000 psi.. Relative strengths of Platinel 2 legs at the same temperature show values of 13,500 psi for alloy 1813 and 8300 psi for alloy 1503. There is no gain in tensile strength offered by the Fibro process in these materials at the 1000°C temperature.

1 (e). Effect of Various Temperatures at the Cold Junction of Chromel-Alumel and Platinel 2 Lead Wire on the EMF Output of the Thermocouple

A. Objective

The objective was to determine the effect of varying temperatures at the junction of noble to base metals on the emf generated by a Platinel 2 thermocouple using Chromel-Alumel lead wire.

B. Equipment

Equipment used included two resistance wire tube furnaces, a multi-position thermocouple switch, a portable potentiometer, and two Variacs. Figure 30 is a photograph of the test set-up.

C. Experimental Method

The hot junction of the test couple was in one furnace while the cold junction was in another furnace. With the hot junction held constant at 1200°C, the lead-wire junction temperature was varied from 0° to 850°C at 50° intervals. At each temperature setting of the lead-wire junction above 0°C, three thermocouple readings were taken; namely, (1) the temperature of the furnace of the hot junction, (2) the temperature of the furnace at the lead-wire junction, and (3) the emf of the test couple. Cold junction correction data were then determined. Only one couple was tested.

To insure a good degree of accuracy in reading the temperature of the system, the Platinel 2 bead was placed in a platinum junction block. Into the same block two Pt. vs. Pt10%Rh couples were inserted; one couple controlled the furnace temperature at 1200°C, while the other was used in conjunction with a potentiometer to insure a temperature of 1200°C (control couple). The

lead-wire junction was located in a second furnace adjacent to a Pt. vs. Pt10%Rh couple. The temperature of the lead wire Platinel 2 junction was varied from 0 to 850°C in 50°C increments.

D. Results

See Table No. 7 and the deviation curve for the results of this phase.

Table No. 7

EMF vs. Temperature Table for Platinel 2 - Chromel-Alumel Lead Wire System

Hot Junctions 1200°C — Reference Junction 0°C

Couple - Lead Wire Junction Temp., °C	EMF of System MV	ΔMV *	% Error Due to Cr-Al Lead Wire
0	49.02	0.02	0.04
50	49.24	0.24	0.49
100	49.26	0.26	0.53
150	49.40	0.40	0.82
200	49.70	0.70	1.43
250	49.70	0.70	1.43
300	49.56	0.56	1.16
350	49.48	0.48	0.98
400	49.40	0.40	0.82
450	49.32	0.32	0.65
500	49.20	0.20	0.40
550	49.03	0.03	0.06
600	48.90	-0.10	-0.21
650	48.66	-0.34	-0.70
700	48.66	-0.34	-0.70
750	48.62	-0.38	-0.[illegible]
800	48.52	-0.48	-0.98
850	48.32	-0.68	-1.39

* Based on an EMF of 49.00 at 1200°C

E. Interpretation of Results

The results show that the use of Chromel-Alumel as lead wire with Platinel 2 is practical, i.e., the error which is introduced by using Chromel-Alumel is of low order. For example, with a lead wire junction temperature of 600 to 700°C, which would be representative of actual aircraft thermocouple probe conditions, the deviation observed was between -0.21 to -0.70 per cent.

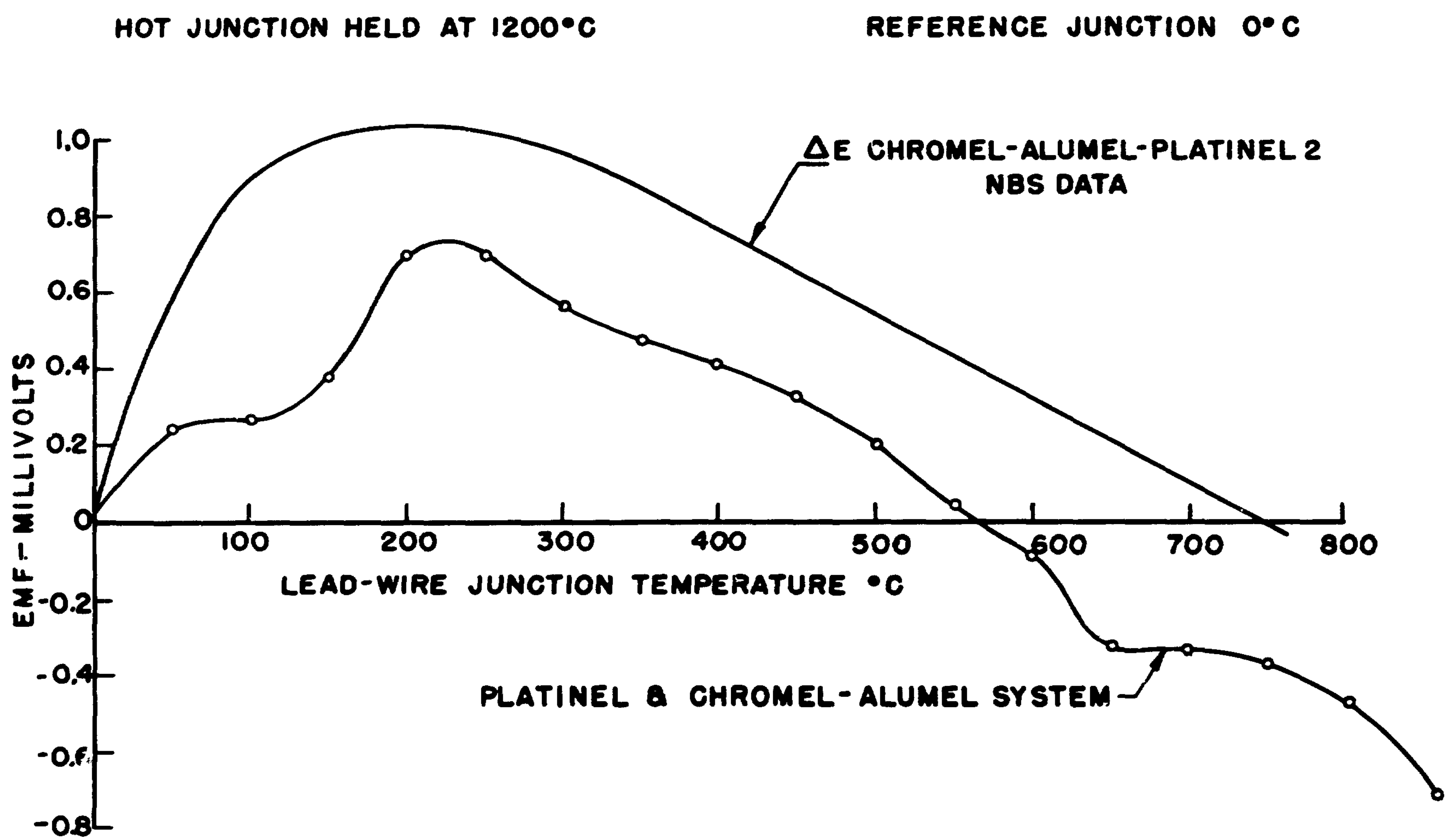

Figure 31. Deviation Curve of Platinel 2 & Chromel-Alumel Lead Thermocouple with Varying Intermediate Junction Temperatures

The figures in the column headed ΔMV are of interest in that when plotted against temperatures, as shown in the graph, the resultant plot has the general characteristics of a plot which relates the emf of Chromel-Alumel minus the emf of Platinel 2 for varying temperatures.

Considering the ΔE Curve of Cr/Al minus Platinel as determined by NBS, there is a steady increase in the Δ E differential which reaches a maximum positive value of 1033 microvolts at 200°C, then decreases steadily finally turning negative.

The greatest deviation has always been found to exist between 150 and 300°C.

2. Investigate the Ability of Platinel 2 to Match Chromel-Alumel to 1500°F (816°C)

A. Objective

To test samples from nine melts of Platinel 2 to see how closely the emf vs. temperature curves will match that of Chromel-Alumel.

B. Equipment

Equipment required for the testing included an Engelhard platinum wire wound alumina tube furnace, West furnace temperature controller, reference junction ice bath, two Leeds and Northrup K-3 Potentiometers, two Leeds and Northrup 2285A Galvanometers, two standard Leeds and Northrup Lamps and Scale, a platinum vs. platinum 10% rhodium furnace control couple, nine Platinel 2 test couples (assembled from nine separate melts of each leg), three NBS reference couples, Fisher Isotemp Oil Bath, Heraeus Platinum Resistance Thermometer, and Degussit Twin Bore Alumina (Minimum Al_2O_3 99.5%) insulators.

C. Experimental Method

The calibration procedure used is similar to that described in Reference 12, Calibration by Comparison Methods, page 9. The emf readings were taken at 50°C intervals from 0°C to 1300°C. See also Appendix I of this report.

Prior to calibration, each leg of the nine sets of Platinel 2 couples was annealed electrically at 1200°C for 15 minutes. In order to eliminate any possible contamination from the binding posts in the strand annealing

rig, the annealed wire was cut back approximately 1 1/2" from each end. Great care was exercised in the assembly of each thermocouple to minimize any straining of the wire. Two bore, high purity Degussit Al-23 insulators were used. The bead of the test couple (made with an oxy-hydrogen torch) was brought into close contact with the bead of the reference couple by wrapping both beads together with platinum foil. The two insulator tubes were then tied together with platinum wire. This system was then inserted about 10" into the furnace, with immersion in the zone of uniform temperature of approximately 6". The effects of conduction along the wires and tubes were practically non-existent. The ends of the furnace tube were plugged to avoid the effects of drafts in the room. The thermocouple reference junction was at 0°C in the ice bath.

With the exception of the readings at 50°C and 100°C which were made in the oil bath, all other determinations were made in the platinum wound furnace at 50°C intervals to 1300°C.

D. Results

The data obtained from the testing of the nine couples, along with previously obtained data, were used to draw up an adjusted emf vs. temperature table. Table No. 8 is the raw experimental data and Table No. 9 is the adjusted emf vs. temperature tabulation. The proposed production tolerance may be seen in Table No. 10.

E. Interpretation of Results

The raw experimental data obtained in these tests, Table No. 8, were evaluated, and an emf vs. temperature was prepared, Table No. 9. A close examination of the experimental data will show that the 400°C point of Couple No. 1, the 500°C point of Couple No. 2, and the 1200°C point of Couple No. 5 were slightly out of the tolerances shown in Table No. 10. After further evaluation of the experimental data, it was concluded that these three isolated points were in experimental error and should be adjusted.

F. Recommendations and Conclusions

The results of the tests performed under this phase indicate that Platinel 2 couples can be manufactured to produce the EMFs shown in Table No. 9 within the tolerance limits shown in Table No. 10. The results of many more melts tend to confirm that the tolerance can be met with ease.

Table No. 8

EMF vs. Temperature Relationship
(Material from 18 Melts)

Thermocouple #	1	2	3	4	5	6	7	8	9
#1503 #1813									
Temp., °C	EMF Millivolts								
50	1.557	1.562	1.558	1.573	1.584	1.590	1.618	1.586	1.592
100	3.299	3.312	3.303	3.336	3.295	3.304	3.343	3.295	3.309
150	5.122	5.161	5.169	5.142	5.167	5.133	5.206	5.147	5.123
200	7.109	7.128	7.115	7.175	7.140	7.174	7.223	7.154	7.162
250	9.192	9.222	9.194	9.269	9.190	9.216	9.289	9.196	9.215
300	11.224	11.379	11.291	11.491	11.273	11.277	11.412	11.281	11.282
350	13.343	13.528	13.462	13.709	13.428	13.436	13.539	13.436	13.467
400	15.566	15.689	15.693	15.943	15.667	15.678	15.763	15.682	15.681
450	17.863	17.965	17.935	18.134	17.913	17.921	17.989	17.973	17.897
500	20.096	20.357	20.184	20.337	20.139	20.182	20.251	20.122	20.152
550	22.332	22.628	22.422	22.622	22.372	22.448	22.512	22.382	22.367
600	24.627	24.793	24.682	24.866	24.617	24.703	24.740	24.637	24.623
650	26.868	27.053	26.897	27.103	26.865	26.961	26.971	26.886	26.879
700	29.082	29.227	29.109	29.293	29.073	29.145	29.208	29.136	29.131
750	31.277	31.374	31.277	31.464	31.241	31.342	31.421	31.282	31.297
800	33.420	33.513	33.403	33.610	33.342	33.485	33.573	33.456	33.452
850	35.496	35.632	35.489	35.703	35.461	35.578	35.680	35.523	35.537
900	37.554	37.685	37.541	37.749	37.498	37.642	37.743	37.573	37.598
950	39.576	39.703	39.536	39.762	39.483	39.640	39.762	39.586	39.598
1000	41.553	41.667	41.492	41.702	41.446	41.603	41.721	41.556	41.548
1050	43.476	43.586	43.417	43.619	43.353	43.524	43.636	43.478	43.460
1100	45.355	45.458	45.268	45.478	45.207	45.387	45.508	45.321	45.323
1150	47.168	47.288	47.081	47.313	47.021	47.203	47.332	47.162	47.142
1200	48.946	49.067	48.849	49.073	48.783	48.974	49.101	48.923	48.907
1250	50.655	50.791	50.556	50.793	50.482	50.681	50.827	50.637	50.620
1300	52.325	52.457	52.205	52.457	52.142	52.333	52.496	52.303	52.281

Table No. 9

Temperature - EMF Relation

for

Platinel 1503 vs. Platinel 1813
(Reference Junction 0°C)

Temp.	M I L L I V O L T S									
°C	0	10	20	30	40	50	60	70	80	90
0	0	.31	.63	.94	1.26	1.58	1.92	2.26	2.61	2.96
100	3.31	3.67	4.04	4.41	4.78	5.15	5.55	5.95	6.35	6.75
200	7.15	7.56	7.97	8.38	8.80	9.22	9.64	10.06	10.48	10.90
300	11.32	11.75	12.18	12.61	13.04	13.48	13.92	14.36	14.80	15.25
400	15.70	16.15	16.60	17.05	17.50	17.95	18.40	18.85	19.30	19.75
500	20.20	20.65	21.10	21.55	22.00	22.45	22.90	23.35	23.80	24.25
600	24.70	25.15	25.60	26.05	26.49	26.94	27.38	27.82	28.26	28.70
700	29.15	29.59	30.03	30.47	30.91	31.35	31.78	32.21	32.64	33.07
800	33.50	33.91	34.32	34.73	35.14	35.56	35.97	36.38	36.79	37.20
900	37.61	38.02	38.43	38.84	39.25	39.66	40.06	40.46	40.86	41.25
1000	41.65	42.03	42.41	42.79	43.17	43.55	43.92	44.29	44.66	45.03
1100	45.40	45.76	46.12	46.48	46.84	47.20	47.56	47.92	48.28	48.64
1200	49.00	49.34	49.67	50.00	50.33	50.67	51.00	51.32	51.64	51.97
1300	52.30									

Table No. 10

Proposed Production Tolerances

Platinel 1503 vs. Platinel 1813

Temperature, °C	EMF (millivolts)	Tolerance (millivolts)
400	15.70	±0.10
500	20.20	±0.10
600	24.70	±0.10
700	29.15	±0.15
800	33.50	±0.20
900	37.61	±0.20
1000	41.65	±0.20
1100	45.40	±0.20
1200	49.00	±0.20
1300	52.30	±0.20

Task No. 2

1. Manufacture of Palladium vs. Platinum-15% Iridium Wire

A. Objective

The objective of this task was to manufacture, i.e., melt, work and calibrate approximately 250 feet of thermocouple grade palladium wire and an equal amount of thermocouple grade platinum-15% iridium wire.

B. Equipment

An induction furnace controlled by a radiation pyrometer was used for melting. The wire was fabricated using swaging and wire drawing equipment. All calibration of thermocouples was done on equipment described in Appendix I. An NBS calibrated platinum vs. platinum-10% rhodium couple was used as the temperature standard. The thermoelement tests were all made against a piece of platinum wire which had been previously compared by NBS to NBS Pt27.

C. Experimental Method

The work under this task consisted mainly in the manufacture and calibration of palladium vs. platinum-15% iridium couples and the comparison testing of each thermoelement vs. Pt27.

The palladium metal and the platinum-15% iridium alloy were melted in an Ajax Induction Furnace. Metals of the highest purity were used. After casting, the bars were worked down to the desired wire sizes by swaging and wire drawing. Care was exercised throughout the processing of these materials to insure that the materials were not contaminated.

All calibrations of thermocouples were performed by the Comparison Method described in Appendix I.

D. Results

The first attempts to produce a palladium vs. platinum-15% iridium couple were made with commercial palladium and commercial platinum-15% iridium wire. A target tolerance of ±3/4% to the NBS tables, Reference 26, was set. Although the match that was obtained with this material was reasonably close to the standard tables, it was decided to prepare a new palladium bar as well as a new platinum-15% iridium bar. The best available platinum, iridium and palladium were used. The usual care that is taken with the processing of thermocouple materials was exercised on these two bars. The finished wire was selected for use in the fabrication of the test probes.

The emf vs. temperature data for test palladium vs. platinum-15% iridium thermocouples are shown in Table No. 11. Data obtained from tests on two Engelhard Industries couples are shown in Columns 1 and 2. The NBS data were obtained from Reference 26.

The emf of the thermoelement palladium vs. Pt27 was determined on the Engelhard Industries palladium.

This data plus the results obtained by NBS (P.D. Freeze[26] et al) are shown in Table No. 12.

Table No. 11

Palladium vs. Platinum 15% Iridium Thermocouples

EMF in Absolute MV Temperature in °C Reference Junction 0°C

	1	2	3
Temp.	Engelhard .040" Dia.	Engelhard .025" Dia.	N.B.S.*
400	9.368	9.359	9.419
500	12.244	12.236	12.317
600	15.356	15.323	15.443
700	18.692	18.647	18.793
800	22.243	22.186	22.364
900	26.002	25.924	26.145
1000	29.957	29.871	30.123
1100	34.071	33.987	34.266
1200	38.339	38.328	38.539

* Reference 26

Table No. 12

EMF, Palladium vs. Platinum (NBS Pt27)

EMF Millivolts, Reference Junction 0°C

Temp. °C	Engelhard	N.B.S.
400	-2.761	-2.753
500	-3.759	
600	-4.940	-4.931
700	-6.309	
800	-7.871	-7.865
900	-9.597	
1000	-11.488	-11.489
1100	-13.522	
1200	-15.689	-15.689

E. Interpretation of Results

The palladium vs. platinum-15% iridium thermocouple materials that were finally prepared and accepted for use in this research program were well within ±0.75% of the mean calibration curve established by NBS for this couple.

NBS data were used as a standard for all work on this phase of the program.

Tests indicated that the surface of the palladium leg may become contaminated during working. Acid cleaning steps usually employed with thermocouple platinum were tried as a means of reducing contamination and were successful.

F. Conclusions

It was shown in the results that a palladium wire could be melted and fabricated to meet the emf vs. Pt27 standard determined by NBS. Based on past experience with diverse thermocouple materials, it is the opinion of the authors that a palladium vs. platinum 15%-iridium couple could be manufactured to a much closer tolerance than that produced for this program.

Task No. 3

1. Investigate the Value of "Fibro" on Reliability, Endurance, and Accuracy of Calibration Over Life in the Palladium vs. Platinum-15% Iridium Thermocouples as well as in Platinel 2

A. Objective

The title of this task summarizes the general objective of the work to be performed. "Fibro", a proprietary process described in Appendix II, was developed to inhibit grain growth in pure metals. The use of this fabrication process has resulted in the production of a high purity platinum with exceedingly good stress-to-rupture properties.

For the purpose of this program, it was decided to check the reliability and endurance by hot tensile and stress-to-rupture tests. This was done and was reported in Item 1 (d). Accuracy of calibration over life or emf stability were tested under this task and are reported here. A direct comparison was made of the hot tensile and stress-to-rupture properties of palladium with those of Fibro Palladium. It was decided to run emf stability tests only on Fibro Pd vs. Pt15%Ir but not on Pd vs. Pt15% Ir since the latter work has been covered by Ihnat and other researchers.

B. Equipment

The equipment for the hot tensile and stress-to-rupture tests is discussed in Section 1 (d). A description of the equipment used in the emf stability or life tests may be found in Section 1 (b). The equipment used for thermocouple calibrations is similar to that described in Appendix I.

C. Experimental Method

Duration tests on two Fibro 1503 vs. Fibro 1813 and one Fibro Pd. vs. Pt15%Ir thermocouples were run for a period of 1080 hours. The thermocouples were aged in air at 1260°C. A .020" diameter wire was used in both Fibro Platinel couples as well as in the Fibro Pd. vs. Pt15%Ir couple. The Fibro materials were fabricated utilizing the method described in Appendix II.

Prior to life-testing, each couple was calibrated over the range of 400°C to 1300°C at 100°C intervals using the calibration procedure described in Appendix I. These couples were then removed from the calibration furnace and were inserted into a tube type (platinum wire wound

on an Al_2O_3 tube) furnace for the aging tests. The depth of immersion was approximately 9" and the constant heat zone was approximately 4". The atmosphere was stagnant air. The bead of the couple plus 1/2" of each leg protruded from the end of the twin bore high purity alumina insulator, and was exposed to the test atmosphere. A platinum vs. platinum-10% rhodium couple was used for control purposes. The bead of this control couple was in direct contact with the test couples.

In order to determine whether any drift in emf had occurred, "in situ" checks on the control couple as well as each of the test couples were made twice daily. At the end of 1080 hours, the test was stopped, and the couples were removed and re-calibrated.

D. Results

Several lots of the Fibro materials were produced. Some of the wires were set aside for use in the fabrication of the test probes in Task No. 4. The emf vs. temperature data of the material intended for this use may be found in Table Nos. 13 and 14. The remaining material was used in determining the emf stability as well as the High Temperature Mechanical Properties (see Task 1 (d)). The results of the emf stability test may be found in Table Nos. 15, 16, and 17. The emf of the Fibro Palladium vs. NBS Pt27 may be found in Table No. 18. For comparison purposes the emf as determined by NBS is shown.

Table No. 13

Stock Material for Task No. 4

EMF vs. Temperature

Fibro Palladium vs. Platinum-15% Iridium

Reference Junction 0°C — Wire Dia. .040"

Temperature, °C	EMF, Millivolts
400	9.364
500	12.247
600	15.358
700	18.698
800	22.256
900	26.016
1000	29.964
1100	34.085
1200	38.351

Table No. 14

Stock Material for Task No. 4

EMF vs. Temperature

Fibro 1503 vs. Fibro 1813

Reference Junction 0°C

Temperature, °C	EMF, Millivolts .040" dia. wire	.025" dia. wire
400	15.637	15.628
500	20.118	20.100
600	24.607	24.633
700	29.071	29.082
800	33.382	33.407
900	37.514	37.545
1000	41.450	41.488
1100	45.232	45.264
1200	48.811	48.847

Table No. 15

EMF Stability Test 1260°C

Fibro 1503 vs. Fibro 1813

EMF - Millivolts
Atmosphere - Air

Wire Dia. .020"
Reference Junction 0°C

Temperature, °C	Before Test EMF	After 1080 Hrs. EMF	Net Change, MV
400	15.698	15.684	-.014
500	20.259	20.274	+.015
600	24.759	24.684	-.075
700	29.198	29.103	-.095
800	33.498	33.382	-.116
900	37.630	37.552	-.078
1000	41.585	41.547	-.038
1100	45.386	45.278	-.108
1200	48.991	48.872	-.119
1300	52.358	52.263	-.115

Table No. 16

EMF Stability Test 1260°C

Fibro 1503 vs. Fibro 1813

EMF - Millivolts
Atmosphere - Air

Wire Dia. .020"
Reference Junction 0°C

Temperature, °C	Before Test EMF	After 1080 Hrs. EMF	Net Change, Δ MV
400	15.718	15.817	+.099
500	20.253	20.342	+.089
600	24.761	24.858	+.097
700	29.252	29.281	+.029
800	33.608	33.578	-.031
900	37.779	37.752	-.027
1000	41.749	41.797	+.048
1100	45.532	45.613	+.079
1200	49.129	49.262	+.133
1300	52.535	52.600	+.065

Table No. 17

EMF Stability Test 1260°C

Fibro Palladium vs. Platinum-15% Iridium

EMF - Millivolts
Atmosphere - Air

Wire Dia. .020"
Reference Junction 0°C

Temperature, °C	Before Test EMF	After 1080 Hrs. EMF	Net Change, Δ MV
400	9.316	9.397	+ .081
500	12.168	12.254	+ .088
600	15.271	15.346	+ .075
700	18.584	18.683	+ .009
800	22.168	22.259	+ .091
900	25.913	26.006	+ .093
1000	29.842	29.952	+ .110
1100	33.959	34.101	+ .042
1200	38.203	38.344	+ .141
1300	42.601	42.702	+ .101

Table No. 18

EMF, Fibro Palladium vs. Platinum (NBS Pt27)

Reference Junction 0°C

Wire Diameter .040"

EMF, Millivolts

Temperature, °C	Engelhard Fibro Pd	(NBS Test)*
400	-2.759	-2.753
500	-3.757	
600	-4.938	-4.931
700	-6.307	
800	-7.872	-7.865
900	-9.597	
1000	-11.491	-11.489
1100	-13.530	
1200	-15.703	-15.689

* Reference 26

E. Interpretation of Results

Since no previous experience in the manufacture of Fibro Palladium, Fibro 1503 and Fibro 1813 had been accumulated, it was decided at the outset not to set any rigid acceptance tolerance on the emf vs. temperature of the matched couples of these materials. The thought was, that if raw materials of the highest purity were used, and the precautions that are usually taken in the fabrication of thermocouple wire were exercised, then the resulting product, though it might not have an emf very close to some established value, would still be usable for the purpose of the experiment. The intent here was, not to see how closely material could be manufactured to some existing emf table, but to determine emf stability and other high temperature properties of new materials having nominal compositions close to those of palladium vs. platinum-15% iridium and Platinel 2 couples prepared by usual routine means. A tolerance of ±1% was set as an informal guide.

An examination of the results in Table Nos. 13 through 18 shows that the emfs developed by the matched Fibro combinations were surprisingly close to established values. Only in one case, shown in Table No. 17, was a

high deviation encountered, and this was within ±1% of the NBS values for Pd. vs. Pt15%Ir.

The materials supplied for the manufacture of probes in Task No. 4 were well within a ±3/4% of established values (Fibro by Engelhard and Pd. vs. Pt15%Ir by NBS), Table Nos. 13 and 14. A remarkably close match to NBS values was obtained with Fibro Palladium as shown in Table No. 18. The net change in emf after testing in air at 1260°C for 1080 hours was negligible for all materials tested.

F. Conclusions

The results of the work on this task were very gratifying. It was shown that Fibro palladium vs. platinum-15% iridium and Fibro Platinel couples could be fabricated to established emf vs. temperature standards. Based on the few emf stability tests made in this project, one can assume that Fibro thermocouples are very stable when exposed to an oxidizing furnace environment at elevated temperatures for approximately 1000 hours. However, much more work will be required to determine the tolerance limits with respect to emf vs. temperature to which these couples can be manufactured. This is also true in regard to stability at elevated temperatures.

Stress-to-rupture and hot tensile tests were performed on Fibro palladium, platinum-15% iridium, Fibro 1503 and Fibro 1813. The results are reported in Item 1 (d). Evaluation of the stress-to-rupture data indicates that there would be no advantage in fabricating the Platinel alloys by the Fibro technique. However, utilizing the same tests, a gain in rupture strength was noted for Fibro palladium at 800 and 1000°C, but not at 1200°C.

A study of the hot tensile data for the same materials showed no clear-cut advantage for the Fibro process over the regular process. The exception here was with Fibro palladium. An increase in hot tensile strength from 4000 psi for the regular palladium to 5000 psi for the Fibro palladium was noted at 1000°C.

An appreciable disparity in high temperature strength was noted in the palladium and platinum-15% iridium wires. When this is related to the apparent relatively high difference in temperature coefficients of expansion of these materials, an explanation may be surmised as to the reason for the failure of the couple when fabricated into a probe. The use of Fibro palladium does not appear to offer a solution to this problem.

Task No. 4

The development of probes of the four basic geometries, namely the stirrup, beaded V, tapered wire V, and coaxial or pencil type of junction also covered various methods of wire size reduction by drawing, swaging, and welding. Many combinations of junction geometry, wire material of either Pd. vs. Pt15Ir or Platinel 2, in either regular or Fibro grades, listed in Table No. 19, were manufactured.

In most cases, thermocouple wires were processed to reduce the cross-section through the ceramic packed portion of the probe in the interest of economical conservation of the precious metal materials.

Two junction wire sizes were used throughout the course of the program, that is .040 and .032 inch diameters, either of which in lengths of less than 3/8 of an inch was adequate to withstand the force of the high temperature combustion gas environment at the 13 lb./ft.^{2} sec. test flow condition.

Probe Nos. 1, 3, 4, 5, 10, 11, 12, 13, 14, 15, 19, 20, 21, 25, 26, 27, 28, 29, and 30 were sent to Aeronautical Systems Division for thermal cycling tests with JP-4 fuel. The remainder were sent to The National Bureau of Standards for response tests, and thermal cycling in a gasoline and air combustion rig.

The results of the tests on the Platinel 2 thermocouples are presented in complete detail in ASD-TDR-62-835.

The first prototype probes were sent to Aeronautical Systems Division for thermal shock testing in the single burner test rig at that facility. Since experimental development work on the palladium vs. platinum 15% iridium couple was in progress at the time, the earliest probes shipped were of the Platinel 2 variety as shown in Table 19.

Exhauster and stack burnout failures at Aeronautical Systems Division limited the amount of testing at the Air Force test facility, and all test couples from No. 30 were sent to NBS for thermal cycling.

None of the Pd. vs. Pt15Ir thermal cycling tests were able to be performed at ASD because of equipment breakdown. Tests were however performed at NBS on 7 couples, Nos. 31-37 inclusive, the results of which are given in ASD-TDR-62-835.

Table No. 19

Description of Probes Produced under Task No. 4

Probe No.	Thermocouple Material	Junction Type	Junction Wire Dia. "D"	Junction Length "C"	Extension Wire Dia. "E"	Wire to Lead Connection	Remarks
1	Platinel 2	Beaded V	.040	0.500	.025	Drawn	
2	Platinel 2	Beaded V	.040	0.500	.025	Drawn	
3	Platinel 2	Beaded V	.040	0.500	.025	Drawn	
4	Platinel 2	Beaded V	.032	0.500	.032	Continuous	
5	Platinel 2	Beaded V	.032	0.500	.032	Continuous	
6	Platinel 2	Beaded V	.032	0.500	.032	Continuous	
7	Platinel 2	Beaded V	.032	0.220	.032	Continuous	
8	Platinel 2	Beaded V	.032	0.310	.032	Continuous	
9	Platinel 2	Beaded V	.032	0.360	.032	Continuous	
10	Platinel 2	Beaded V	.040	0.250	.025	Torch Weld	
11	Platinel 2	Beaded V	.040	0.250	.025	Torch Weld	
12	Platinel 2	Beaded V	.040	0.250	.025	Torch Weld	
13	Platinel 2	Stirrup	.040	0.312	.025	Torch Weld	
14	Platinel 2	Stirrup	.040	0.375	.025	Torch Weld	
15	Platinel 2	Stirrup	.040	0.500	.025	Torch Weld	
16	Platinel 2	Stirrup	.040	0.312	.025	Torch Weld	
17	Platinel 2	Stirrup	.040	0.312	.025	Torch Weld	
18	Platinel 2	Stirrup	.040	0.312	.025	Torch Weld	
19	Platinel 2	Tapered V	.040-.025	0.280	.025	Torch Weld	
20	Platinel 2	Tapered V	.040-.025	0.312	.025	Torch Weld	
21	Platinel 2	Tapered V	.040-.025	0.375	.025	Torch Weld	
22	Platinel 2	Tapered V	.040-.025	0.220	.025	Torch Weld	
23	Platinel 2	Tapered V	.040-.025	0.312	.025	Torch Weld	
24	Platinel 2	Tapered V	.040-.025	0.375	.025	Torch Weld	
25	Pd/Pt15%Ir	Beaded V	.040	0.312	.025	Swaged	
26	Pd/Pt15%Ir	Beaded V	.040	0.312	.025	Swaged	
27	Pd/Pt15%Ir	Beaded V	.040	0.343	.025	Swaged	

Table No. 19 - (Cont'd.)

Probe No.	Thermocouple Material	Junction Type	Junction Wire Dia. "D"	Junction Length "C"	Extension Wire Dia. "E"	Wire to Lead Connection	Remarks
28	Pd/Pt15%Ir	Stirrup	.040	0.375	.025	Swaged	
29	Pd/Pt15%Ir	Stirrup	.040	0.312	.025	Swaged	
30	Pd/Pt15%Ir	Stirrup	.040	0.312	.025	Swaged	
31	Pd/Pt15%Ir	Stirrup	.040	0.250	.025	Swaged	Fibro Pd
32	Pd/Pt15%Ir	Stirrup	.040	0.312	.025	Swaged	Fibro Pd
33	Pd/Pt15%Ir	Stirrup	.040	0.375	.025	Swaged	Fibro Pd
34	Pd/Pt15%Ir	Tapered V	.040-.025	0.312	.025	Swaged	Fibro Pd
35	Pd/Pt15%Ir	Beaded V	.040	0.375	.025	Swaged	Fibro Pd
36	Pd/Pt15%Ir	Stirrup	.040	0.250	.025	Heli-arc Weld	
37	Pd/Pt15%Ir	Stirrup	.040	0.438	.025	Heli-arc Weld	
38	Platinel 2	Stirrup	.040	0.250	.025	Swaged	Fibro
39	Platinel 2	Stirrup	.040	0.312	.025	Swaged	Fibro
40	Platinel 2	Stirrup	.040	0.312	.025	Swaged	Fibro
41	Platinel 2	Beaded V	.040	0.250	.025	Swaged	Fibro
42	Platinel 2	Beaded V	.040	0.312	.025	Swaged	Fibro
43	Platinel 2	Beaded V	.040	0.312	.025	Swaged	Fibro
44	Platinel 2	Tapered V	.040-.032	0.250	.032	Swaged	Aspirating Cap
45	Platinel 2	Tapered V	.040-.032	0.250	.032	Swaged	Aspirating Cap
46	Platinel 2	Tapered V	.040-.032	0.312	.032	Swaged	Aspirating Cap
47	Platinel 2	Coaxial	See dwg.	0.220	.032	Continuous	
48	Platinel 2	Coaxial	See dwg.	0.280	.032	Continuous	
49	Platinel 2	Coaxial	See dwg.	0.312	.032	Continuous	
50	Platinel 2	Coaxial	See dwg.	0.312	.032	Continuous	
51	Platinel 2	Coaxial	See dwg.	0.250	.032	Continuous	Aspirating Cap
52	Platinel 2	Coaxial	See dwg.	0.250	.032	Continuous	Aspirating Cap
53	Platinel 2	Coaxial	See dwg.	0.312	.032	Continuous	Aspirating Cap

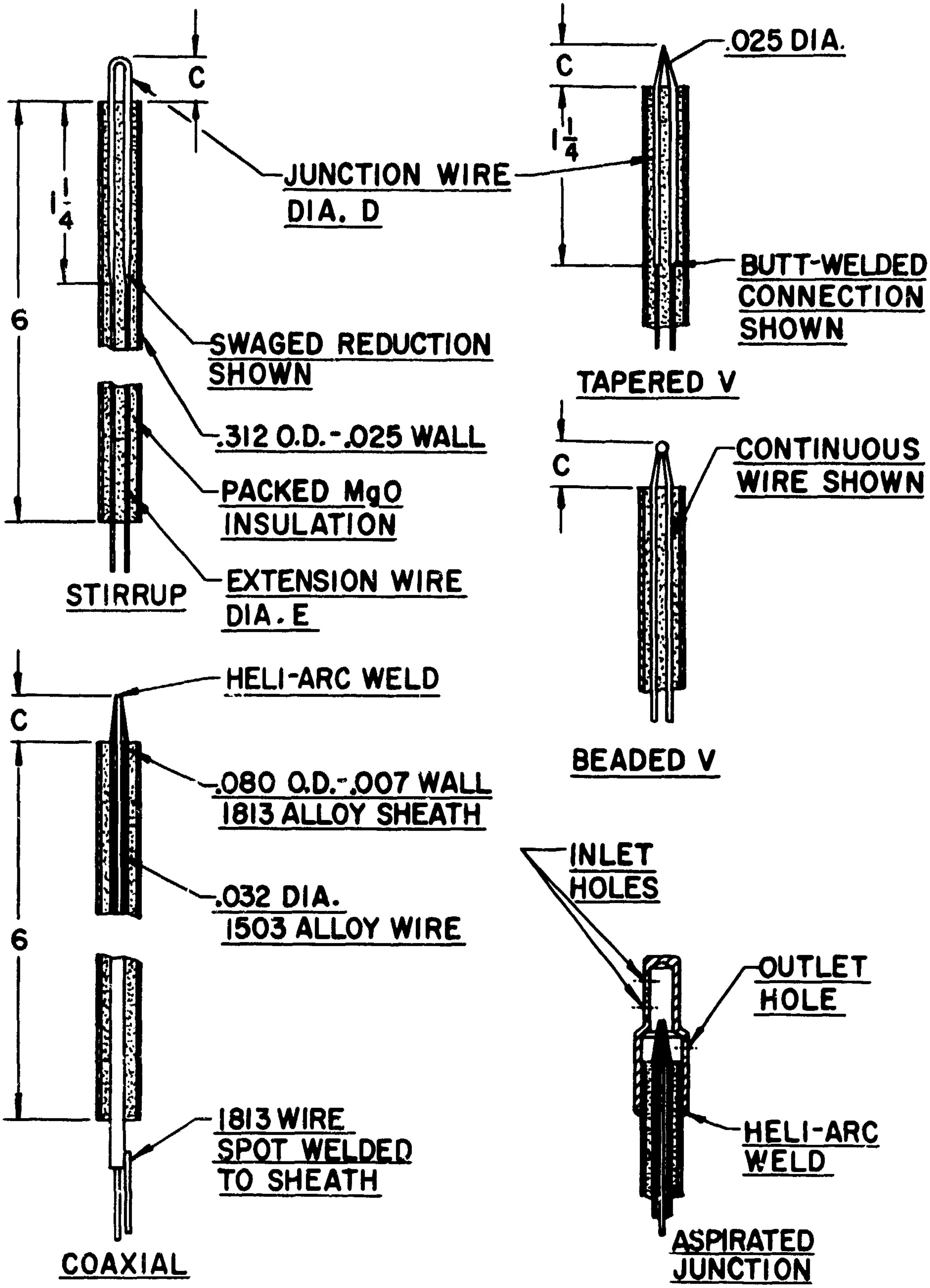

Figure 32. Types of Thermocouple Probe Geometries Investigated Under Task No. 4

The thermocouple junctions were oriented in these tests so that the plane of the wires was always normal to the direction of the gas flow. The temperature change to which these couples were subjected was about 300°F. A summary of the results of these tests is given in the following table:

Table No. 20

Experimental Time Response Data

Couple No.	Average time τ, in Seconds — Gas Temp. - 1000°F, Gas Flow lbs./ft.^{2} sec. 6	8	Gas Temp. - 1600°F, 6	8
31	0.87	0.80	0.73	0.68
32	0.77	0.71	0.69	0.64
33	0.85	0.78	0.70	0.62
34	0.61	0.54	0.53	0.42
35	0.91	0.87	0.79	0.70
36	1.31	1.14	1.12	1.08
37	0.91	0.76	0.73	0.64

A summary of the results of the calibration of these couples is presented in the following table:

Table No. 21

EMF Output of the Following Thermocouple Probes

Temp. °F	31	33	34	35	36	37
	mv					
200	1.792	1.790	1.791	1.791	1.793	1.792
400	4.253	4.249	4.251	4.246	4.252	4.254
600	6.971	6.976	6.971	6.979	6.983	6.986
800	9.944	9.951	9.948	9.960	9.963	9.965
1000	13.189	13.205	13.200	13.208	13.214	13.213
1200	16.703	16.723	16.719	16.716	16.735	16.728
1400	20.496	20.530	20.522	20.537	20.538	20.527
1500	22.496	22.540	22.535	22.541	22.548	22.529
1600	24.566	24.609	24.607	24.610	24.617	24.595
1700	26.682	26.740	26.737	26.749	26.747	26.715
1800	28.887	28.950	28.946	28.952	28.952	28.906
1900	31.124	31.194	31.191	31.192	31.189	31.137
2000	33.409	33.493	33.487	33.490	33.481	33.418
2100	35.740	35.825	35.822	35.825	35.803	35.741
2200	38.103	38.191	38.187	38.181	38.172	38.098
2300	40.488	40.584	40.586	40.586	40.560	40.474

Following the calibration of these thermocouple probes in the muffle furnace, they were subjected to tests in the thermal shock apparatus. During installation in the apparatus one of the lead wires of probe No. 37 broke, and it was replaced by probe No. 32.

The temperature of the exhaust gases was adjusted so that the probes reached a temperature of 2000°F. The mass flow of the exhaust gases was held at 13 lbs. per $ft.^2$ sec.. The thermal shock cycle consisted of nine minutes in the exhaust gas stream followed by three minutes in cool air at a very low velocity, probably less than 50 ft. per sec.

All thermocouples failed in a relatively short period of time. No. 36 developed an open circuit during the heating of cycle No. 23. Nos. 34, 32, 33, 31, and 35 failed during cycles 58, 67, 67, 81, and 109 respectively. The two V-type junctions, Nos. 34 and 35 failed in the palladium element near the swaged insulating material. The stirrup-type thermocouples failed nearer the junction and in some cases in both elements. (End of NBS report).

As previously mentioned in Summary of Results, all of the junction failures in the Pd vs. Pt15%Ir couple had a characteristic physical appearance in the pronounced elongation of the positive palladium leg. The exact reason for the failure is not known, though it is fairly evident by the appearance of the relatively sharp fractures of the wires, that fatigue is not the cause of the breaks. A more likely reason would seem to be in rapid grain growth which occurs in the pure element in comparison to that observed in an alloy.

The markedly different tensile strengths and coefficients of expansion of palladium and platinum 15% iridium wires at elevated temperature, coupled with rapid growth of grain structure, may well have influenced the results observed.

Three Pd vs. Pt15%Ir probes, which had been tested on Contract No. AF33(600)-32302, and which failed after relatively short time in the single burner rig were examined. A sample of the palladium in the vicinity of the break was assayed for sulfur analysis. It was determined that 0.24% S was present. The opinion was expressed that this is an exceptionally high concentration of sulfur, sufficient to cause embrittlement and subsequent failure of the palladium wire.

Numbers of failures of wire occurred in the Platinel 2 probes during the severe thermal shock treatment of the temperature cycling, all of the failures occurring internally. The breaks in the wires generally coincided with lateral cracks across the ceramic insulation, suggesting that they might have been due to differential expansion between the ceramic and wire.

Failures were also noted at the areas close to internal welds between wires of .040 and .025 diameters.

Increasing the wire size from the .025 diameter within the body of the probe to .032 or .040 eliminated the failure problem.

Recommendations

1. Additional work as to the reason for calibration shifts at aging temperatures in excess of 1200°C appears to be warranted. This would include chemical assaying and spectrographic analysis to establish possible changes in the nominal mixture ratio of elements in each alloy, as well as to determine the presence of contaminating influences.

2. Further study of aging treatment of wire should be made to develop a stabilizing procedure for continuous thermocouple usage at the higher temperature limit. This would include testing for the effects of high temperatures on larger wire sizes.

3. The effects of severe cold working on wire metallurgical structure should be investigated. The results shown by the thermal shock tests on wire reduced by drawing or swaging from .040 dia. to .025 dia. point to the need for this information.

4. More detailed metallurgical study of welding of noble-to-base metals as in the case of alloy 1813 to chromel, and alloy 1503 to alumel is a serious need. Industry is faced with this problem because of economic considerations in conservation of the precious metals.

5. A tabulation of emf vs. temperature similar to the NBS Table 561 would prove most useful to the aircraft industry at this time.

6. An extension of the temperature limit of the gold-palladium-platinum alloy thermocouple system for higher performance engines suggests continuing research and development with Platinel-like materials.

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APPENDIX I

Calibration Method

This method was originally developed at the National Bureau of Standards for the comparison calibration of two thermocouples. A simultaneous reading is taken of the emf of each of the couples without waiting for the furnace to come to a constant temperature. In order to insure equality of temperature between the measuring junctions of the thermocouples, they are usually welded together. However, for this project an alternate joining method was employed. The beads of the test and standard couples were wrapped together with platinum foil.

A separate potentiometer was used to measure each emf, one connected to each thermocouple. Each potentiometer was provided with a reflecting galvanometer. The two spots of light were then reflected onto a single scale, the galvanometers being set in such position that the spots coincide at the zero point on the scale when the circuits are open and, therefore, also when the potentiometers are set to balance the emf of each thermocouple. Simultaneous readings were obtained by setting one potentiometer to a desired value and adjusting the other so that both spots of light pass across the zero of the scale together as the temperature of the furnace is raised or lowered. A calibrated platinum vs. platinum-10% rhodium couple was used as a standard.

Figure 3 is a schematic of the calibration equipment and Figure 4 is a photograph of this equipment.

APPENDIX II

"Fibro" Thermocouple Wire

Experience has shown that in platinum vs. platinum/rhodium thermocouples subjected to appreciable handling, the life of the couple is frequently determined by the resistance of the pure platinum element to stresses set up during handling. Thus, in couples that fail for reasons other than contamination or loss of "calibration", by far the greatest percentage fail by fracture of the pure platinum element. This is, of course, in accordance with the known mechanical weakness of pure platinum after prolonged heating at high temperatures, and which is associated with excessive grain growth. The grain growth is particularly marked in thermoelement platinum on account of its extreme purity.

It has not been found possible hitherto to effect any control of grain growth in the case of thermoelement quality platinum, as the powder metallurgical techniques which might be used to effect an improvement are unsuitable for manufacturing thermoelement quality platinum.

However, by the use of an entirely new principle, Reference 29, a thermoelement quality platinum wire can be prepared having a fibrous structure which resists recrystallization at elevated temperatures and which shows a marked resistance to grain growth. Notwithstanding the enhanced mechanical properties, temperature coefficient of resistance and thermoelectric tests have shown this new thermocouple platinum, designated "Fibro Thermocouple Platinum", to be indistinguishable from conventional thermoelement platinum as far as thermoelectric behaviour is concerned.

Time-to-rupture tests carried out at high temperatures have revealed Fibro thermoelement to be many times better than normal thermoelement. Thus, in one series of tests, carried out at a temperature of 1450°C under a stress of 171 lbs./sq. in., normal thermocouple platinum fractured after 2 hours, while 300 hours elapsed before the Fibro thermoelement fractured.

By use of the Fibro thermoelement platinum, it is now possible to form a thermocouple in conjunction with a conventional platinum-rhodium thermocouple alloy in which the two elements are more nearly compatible in terms of mechanical properties and, in situations where mechanical strength is important, the couple has a longer life than one employing conventional elements.

The idea of using the Fibro technique to improve the high temperature properties of relatively weak thermoelements was carried over to this project. The immediate objective was to try to improve the strength of the palladium. At the same time it

was tried on Platinel to see what effect it would have on its properties. The results of the tests on finished Fibro materials are reported elsewhere in this report (Tasks 1 (d) and 3,1).

Method of Preparing Fibro

Fibro materials made for this contract were made in a manner which is similar to the one described below.

Metals of the highest commercial purity were selected. Spectrographic analysis was the criterion. The selected material was melted and cast. The bar was then cold worked to 1/2" diameter and cut in half. One-half was worked down to .020" diameter wire with appropriate acid cleaning steps to insure the continued purity of the material. A sample of this wire was checked at 1200°C against a calibrated platinum wire to determine whether its thermal emf met certain requirements. After approval of the wire, a convenient length of the first half of the bar was bored to produce a tube having a 1/8 inch wall thickness. The .020 inch diameter wire was cut in lengths equal to that of the tube and straightened. The tube and the wires were boiled in aqua reqia, washed in distilled water and dried, taking precautions to preclude any possibility of recontamination. Using clean gloves to protect against impurity pick-up, the wires were packed into the tube to form as complete a packing as possible. The composite bar was repeatedly swaged and annealed until the final wire was formed. All possible precautions were taken to prevent contamination. After all work was completed, the final wire was recalibrated. No noticeable change in emf was detected. Some of the results of the electrical tests on these materials are reported under Task No. 3.

Manufacturing Technique Report
Addendum to Final Report

on

Applied Research, Fabrication
and Testing of 2300°F Thermocouples
for Air-Breathing Propulsion Systems

Propulsion Laboratory
Aeronautical Systems Division
Air Force Systems Command
Wright-Patterson Air Force Base, Ohio

Project No. 3066   Task No. 30245

Prepared under Contract No. AF 33(616)-7825
by Engelhard Industries, Inc.
Instruments and Systems Section
by Herbert J. Greenberg

Introduction

The development efforts associated with the manufacture of actual hardware under Task No. 4 were:

1. Swaging techniques.
2. Wire reduction by swaging.
3. Electrical butt-welding of wire.
4. Torch butt-welding of wire.
5. Heli-arc butt-welding of wire.

Swaging

All of the thermocouple assemblies manufactured under this contract were processed using crushable bead insulators of magnesium oxide. Outside diameter of all probes was held constant at 0.312 dia. Sheath material was also the same in all cases, being Inconel of seamless drawn variety, having a No. 1 temper (annealed). Wall thickness of the tubing as procured was .025 inches.

A Torrington No. 3 swager was used to manufacture all probes; this size machine is just adequate to accommodate the 0.375 O.D. of the unswaged sheath. All swaging was fed by hand at a rate of approximately 1/2 inch per second.

The first lots of swaged thermocouples used insulators of 0.295 dia. Some cases of poor packing of insulation resulted from this use of apparently undersized insulators. Voids were found in the earliest sample probes, permitting seepage of oil by capillary action, resulting in low insulation resistance and some internal wire failures.

Immediate improvement in the density of packing was noted upon increasing insulator size to 0.310 O.D. The reduction of area of the insulation from the initial diameter of 0.310 to its final size of approximately 0.256 amounts to 32% (sheath wall thickness increases slightly to .028 during swaging).

Greater density of pack has been tried by using tubing with .035 wall thickness. The reduction in area in this case, assuming a wall buildup of .005, amounts to --

$$100 \frac{0.310^2 - 0.232^2}{0.310^2} \approx 45\%$$

A noticeable decrease in wire size results from the use of this percentage reduction in area. Accordingly, a reduction of 30 to 35% is recommended.

Powdering-out of insulation is prevented by providing end-wise confinement of the insulation with teflon plugs. The plugs are locked in position by swaging opposite ends of the

tubing prior to the final pass. Clearance holes of approximately .044 dia. are provided for passage of the .040 thermocouple wires, the O.D. being sized to give a slight press fit into the sheath material. The plugs are easily removed by slitting the sheath with an abrasive cut-off wheel, and sliding them off the wires.

Some tests were run using nylon plugs, but this material grips the wire, and is difficult to remove. Experiment with larger clearance holes may find the nylon plugs to be equally as effective as the teflon ones.

The operations shown in Figure 33 illustrate the standard swaging procedure which has evolved from a variety of techniques attempted. The method is useful in fabricating, not only the simple beaded V junction illustrated, but also the loop and tapered wire junctions as well. In the latter cases, the junctions are pre-formed prior to assembly, and are enclosed over their length by powdered MgO for a short distance to the close teflon plug.

This swaging procedure was developed primarily to permit assembly of probes with wires of varying cross-section as well as dissimilar lead-wire materials. If the wires were to be of uniform diameter and material, there would be no need for this more involved technique. They would merely be sectioned from a long length of swaged "stock". The saving of precious metal through the use of this technique is appreciable enough to warrant its use.

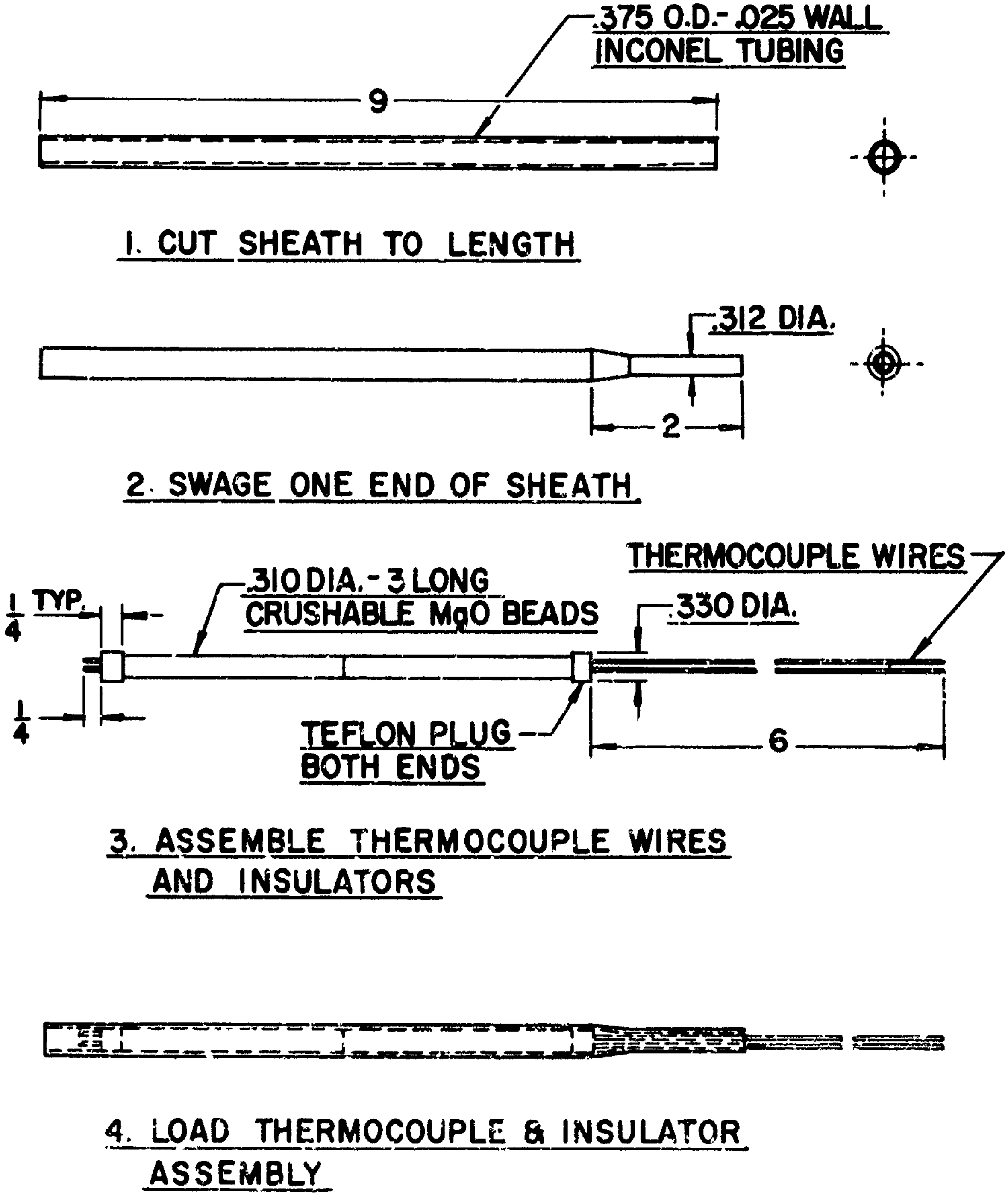


Figure 33. Operations Analysis of Thermocouple Fabrication

SHEET 1 OF 2

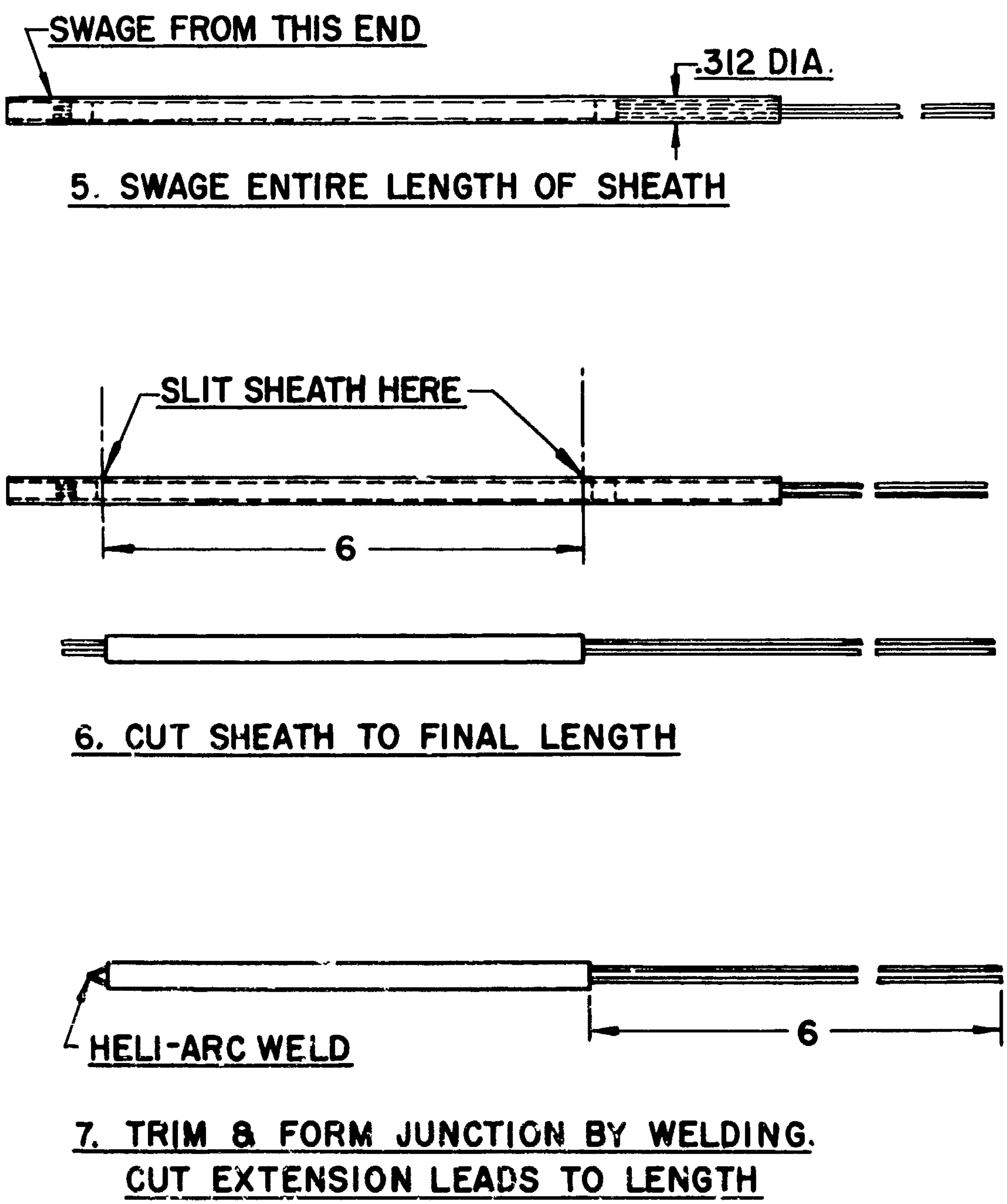


Figure 33 (Cont'd)

SHEET 2 OF 2

Wire Reduction

Extensive efforts were devoted to the reduction in wire size from .040 inch diameter to .025 inch diameter by various techniques in the interest of economy of noble metal usage in thermocouple probe construction.

Probes were fabricated and submitted to testing to both ASD and NBS with one and two-piece thermocouple leads. The one-piece leads were reduced from the .040 inch to .025 inch size by either drawing in three passes, or by swaging in one pass.

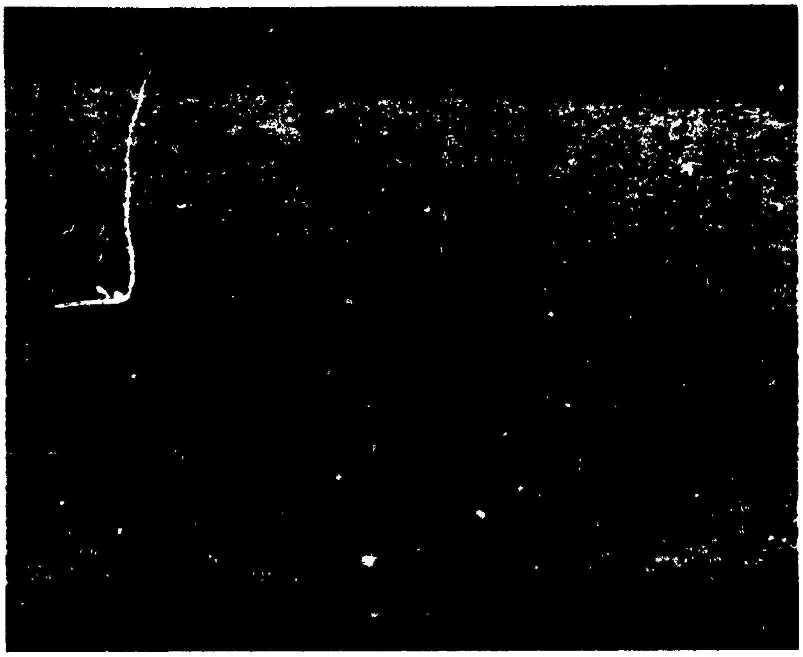
As far as the drawing technique is concerned, no particular problem was met, though the effort is hardly worth the time required, and is not recommended for further consideration.

Reduction of area by swaging was investigated. The earliest experience was obtained using the No. 3 swager, and considerable difficulty was encountered due to the condition of the machine. Deterioration in the necessarily tight clearances between die blocks and the spindle slot resulted in work having poor surface finish due to "shaving" or "finning". Since the larger swaging machines have relatively large built-in clearances, it is difficult to obtain satisfactory wire reduction below a certain size. The smaller swagers are constructed with the fine clearances required to produce light work. Samples of Platinel 2 wire of .040 inch diameter sent to The Torrington Company were processed on their light Model #100, being reduced in one pass to .025 inch diameter. This is equivalent to a reduction in area of 61%. The success of the tests resulted in purchase of this model, and no trouble was experienced in reducing the Platinel 2 alloys, palladium, or even the considerably harder platinum 15% iridium material in one pass. Surface finish was always excellent, and the wire emerged from the machine in straight condition.

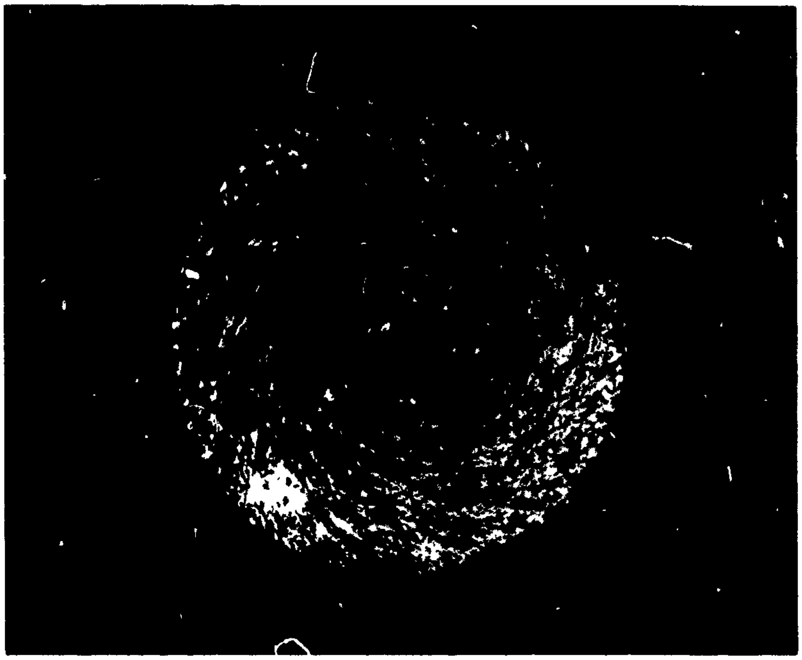
The operation of wire reduction for the approximate 12 inch length used, required about 15 seconds, and the length of the reduced section can be controlled very precisely with little effort.

The results of the tests on probes having wires swaged from the .040 inch diameter to .025 inch diameter leave question as to the severity of the cold-work within the wire. The last tests performed at NBS used wires reduced at the most by 36%. There were no failures under the thermal-shock conditions to 700 cycles in the last six probes tested.

Figure No. 34 illustrates a micro-etch cross-section of a Platinel 2 alloy 1503 wire reduced in one pass from .040 inch to .025 inch diameter. The spiral grain flow effect is no doubt



Longitudinal Section



Cross Section

Figure 34

Micro-Etch Section of .025 Diameter Platinel 1503 Alloy
Reduced by Swaging in One Pass

Original Diameter .040 in.   Magnification 100X

due to the twist exerted by the operator in feeding the wire through the dies. It would be interesting to compare wire cross-sections from samples swaged in say three passes with intermediate anneals.

More work in this area in consideration of the results appears to be warranted.

Butt-Welding of Lead Wires

1. <u>Electrical Butt-Welding</u>

An attempt at using DC capacitive discharge welding equipment to butt-weld Platinel 2 wires was made by a local manufacturer of such equipment without success. This experimentation was dropped when immediately satisfactory results were obtained with AC synchronous welding equipment. The relatively long cycle time (approximately 1 1/2 cycles) followed by pulses of current to anneal the weld area produced strong welds.

2. <u>Torch Welding</u>

Torch butt-welds on both legs of Platinel 2 wires have been made using a fine torch tip supplied with city gas and oxygen. The wires are supported in "V" grooves machined in a graphite block the grooves being separated by a recess at the area of the junction. The heat is applied to the heavier wire close to its end. The color temperature of both wires is closely observed, and the position of the flame tip is adjusted to maintain the same color in both wires. Once the wires reach plasticity, slight endwise pressure on one wire will bring about fusion at the junction.

3. <u>Heliarc Butt-Welding</u>

Very smooth butt-welded joints have been made on all four wire materials investigated under this program, that is, Platinel 2 alloys, 1813 and 1503, palladium, and platinum 15% iridium. The wires are supported in the same carbon block. The arc is struck with a tungsten electrode of 1/32 inch diameter, direct current being used, and gradually worked over towards the joint. As the joint area melts and fuses, the arc is broken by removal of the electrode to approximately 1/2 inch from the wire, while maintaining the flow of helium.

DC current requirement is 8-10 amps. Helium flow rate is 30 cu. ft./hr. The weld bead formed at the junction is removed by swaging, the excess material blending into the tapered transition zone between the .040 inch and .025 inch diameters. This is done with an .025 inch diameter wire reducing die.

This same heliarc butt-welding technique can be used to form the junction of the two .040 inch diameter wires of the stirrup type design shown in Figure 32. Removal of the excess bead material at the joint is accomplished by swaging with an .040 inch diameter die.

Annealing Procedures

All Platinel 2 wires were annealed at 850°C following preparation for assembly into probes. The finished probes were likewise annealed at 850°C for the purpose of strain relieving and stabilization prior to calibration.

Palladium vs. platinum iridium wires or probes were annealed by heating to 1200°C for one hour in an atmosphere of argon.

Probe Fabrication

1. Stirrup Type Junction

Thermocouple wires were butt-welded as the first operation in the processing of this junction configuration. After forming the junction shape by bending over a mandrel, the insulators were slid into position and the thermocouple and insulator assembly were otherwise processed in accordance with the steps outlined in Figure No. 33.

2. Tapered "V" Junction

Thermocouple wires were prepared by tapering the junction ends in a die having an .040 - .025 inch reduction in diameter. The mating surfaces of the wires were prepared by filing. The junction was then made by spot-welding, a minimum of two spots being used. Assembly operations were otherwise in accordance with the procedure outlined in Figure No. 33.

3. Beaded "V" Thermocouple

The processing technique for this thermocouple follows in detail the outline shown in Figure No. 33. Formation of the junction is facilitated through the use of a graphite chill block, which serves to control the junction length effectively. The thermocouple wires are cut to a length greater than the width of the chill-block, allowance being made for the anticipated volume of the bead. Experiment will establish the exact length of wire required to produce a finished junction length.

Prior to welding, the wires are bent to the triangular plan-form with the last 1/8 of an inch or so being in tangential contact from the first point of intersection.

The two wires are held in contact with the carbon chillblock during the welding operation. The arc is struck at approximately half an inch from the wires, and is moved to the junction. Once fusion has occurred, the arc may be removed.

Aeronautical Systems Division, Dir/Aeromechanics, Propulsion Lab, Wright-Patterson AFB, Ohio

Rpt. Nr ASD-TDR-62-891; APPLIED RESEARCH, FABRICATION AND TESTING OF 2300°F THERMOCOUPLE FOR AIR-BREATHING PROPULSION SYSTEMS; Final Report, Jan 63, 84p.incl. illus. tables, 29 refs.

Unclassified Report

Development work on two thermocouple systems for use in aircraft jet engines to temperatures of 2300°F is herewith reported. The two couples involved are the palladium vs, platinum 15% iridium previously investigated under USAF contract No. AF 33(600)-32302, and Platinel 2, a propietary material produced by Engelhard Industries, Inc.

(over)

Reliability of the latter thermocouple in the jet-engine environment is shown.

Fabrication techniques for manufacture of four basic thermocouple geometries as well as performance data for same are presented.

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2. Sensors
3. Temperature Sensing Systems
4. Propulsion

I. AFSC Project 3066 Task No. 306602

II. Contract AF 33(616)-7825

III. Engelhard Industries Inc.Newark, N.J

IV. H.J. Greenberg and E.B. Zysk

V. Not Aval Fr OTS

VI. In ASTIA Collection

Aeronautical Systems Division, Dir/Aeromechanics, Propulsion Lab, Wright-Patterson AFB, Ohio

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